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Electrochemical Processes in Chemical Industries

ELECTROCHEMICAL PROCESSES IN CHEMICAL INDUSTRIES

by

ALBERT REGNER

D. Sc.

ARTIA • PRAGUE

ELECTROCHEMICAL PROCESSES IN CHEMICAL INDUSTRIES

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LIST OF SYMBOLS

a	Chemical activity.
A	Unit of electric current, ampere.
A	Atomic weight.
c	Concentration defined in moles per liter (molarity).
c_e	Concentration defined in gram-equivalents per liter.
C	Unit quantity of electricity, coulomb (3.10^9 electrostatic units of charge).
D	Diffusion coefficient.
e	Chemical symbol of electron, or also Charge of an electron ($1.6 \cdot 10^{-19}$ coulombs).
E	Voltage (in volts), mostly electromotive force of a cell.
E_p	Polarization voltage.
E_R	Decomposition voltage.
EMF	Electromotive force of a cell.
f	Fugacity.
f_A	Conductance coefficient.
F	Unit quantity of electricity, faraday, 96500 coulombs.
h	Planck's universal constant ($6{,}624.10^{-27}$ erg./sec.)
H	Enthalpy.
I	Current in amperes.
I_h	Current density on the electrodes.
K	Equilibrium constant.
K_s	Ionic solubility product.
K_v	Ionic product of water.
ln	Natural logarithm.
log	Decadic logarithm.
m	Concentration defined in moles per 1000 g of solvent (molality).
n	Number of gram-equivalents undergoing electrochemical reaction.
N	Normal concentration (normality).
N	Power.
N	Avogadro's number ($6{,}023.10^{23}$).
N	(with subscript) Concentration defined in terms of the mole fraction.
p	Gas pressure.

pH	Negative decadic logarithm of the H_3O^+ activity (hydrogen ion exponent).
q	Quantity of electricity.
Q	Heat evolved by the system or supplied to the system.
R	Ohmic resistance.
R	Gas constant (8,314 joule/mole grad).
S	Entropy.
t	Time.
t	Temperature in °C
t	(with subscript). Transference number of an ion.
T	Absolute temperature in °K.
v	(with subscript). Velocity of ions under unit potencial gradient.
V	Unit of potential (volt).
z	Number of elementar charges of an ion (valence).
W	Work (energy).
α	Degree of dissociation; electrochemical equivalent.
γ	Activity coefficient.
δ	Thickness of the diffusion layer.
ε	Elementary quantum of energy. ($\varepsilon = h\nu$).
ε	Oxidation electrode potential.
ε_K	Liquid junction (diffusion) potential.
φ	Volume of the solution in millilitres containing one gram-equivalent of an electrolyte.
η_I	Current efficiency.
η_w	Energy efficiency.
$\varkappa$	Specific conductivity.
λ	(with subscript) Ionic conductance.
Λ	Equivalent conductivity.
μ	Chemical potential.
μ	Molar conductivity.
μ	Ionic strength.
ν	(with subscript) Number of ions arising from one molecule of electrolyte.
ν	Frequency of electromagnetic radiation.
π	Reduction electrode potential.
ρ	Specific resistance; density.
Σ	Summation.
ω	Overvoltage.
Ω	Unit of electrical resistance, ohm.

I. INTRODUCTION TO ELECTROCHEMISTRY

A. A SURVEY OF THE ATOMIC AND MOLECULAR THEORY

Elements are built of atoms the components of which are the protons (a positively charged hydrogen nucleus of the mass $m = 1.67 \times 10^{-24}$g and a charge $+e = 1.60 \times 10^{-19}$ coulombs), the neutrons (a particle with the mass equalling approximately that of a proton, but without any electric charge), and the electrons (an atom of negative electricity, 1837 times lighter than the proton, with the mass $m = 9.11 \times 10^{-28}$g; its electric charge is of the same value as that of the proton, however with an opposite sign).

Individual atoms of elements vary in number and configuration of these elementary particles, while the total number of electrons and protons is the same, so that the whole is electroneutral to the outside. Elements can be arranged in a series, according to the number of protons in the nucleus (or electrons), in which the following member has always one proton more, than the previous one. The ordinal or atomic number of elements is determined by the number of protons which in turn decides their position in the periodic system.

In the nuclei of atoms neutrons are concentrated, in addition to protons; the presence of neutrons in the nucleus does not change the ordinal number of the element, but it contributes to the growth of its atomic weight. Elements having the same number of protons, but differing in the number of neutrons, are called isotopes. Electrons, being practically particles almost without any mass, move in eliptical paths in one or several shells round the nucleus approximately in the same manner as the planets move round the sun.

In each shell, or on each level (marked by letters K, L, M, N, O, P, Q) only a very definite number of electrons can move as a maximum. As can be seen from Table 1, where Z is the atomic number of each element, the innermost shell is fully saturated with two electrons already. On the highest outer levels the maximum of eight electrons (the octet) can move.

The chemical and electrochemical characteristic properties of elements are determined by the electrons in the last outer shell. Elements with outer levels filled to completion, i. e. the rare gases (helium, neon, argon, crypton, xenon and radon), are noted for the great stability of their electronic structures; atoms of such elements, known for their chemical inactivity, do not show any tendency to form molecules, neither in mutual bonds nor in bonds with other atoms.

In all other elements the outer shells are not fully occupied by electrons; such

Table 1. Periodic system of elements

Z	Element	K	L	M	N	O	P	Q
1	H	1						
2	He	2						
3	Li	2	1					
4	Be	2	2					
5	B	2	3					
6	C	2	4					
7	N	2	5					
8	O	2	6					
9	F	2	7					
10	Ne	2	8					
11	Na	2	8	1				
12	Mg	2	8	2				
13	Al	2	8	3				
14	Si	2	8	4				
15	P	2	8	5				
16	S	2	8	6				
17	Cl	2	8	7				
18	A	2	8	8				
19	K	2	8	8	1			
20	Ca	2	8	8	2			
21	Sc	2	8	9	2			
22	Ti	2	8	10	2			
23	V	2	8	11	2			
24	Cr	2	8	13	1			
25	Mn	2	8	13	2			
26	Fe	2	8	14	2			
27	Co	2	8	15	2			
28	Ni	2	8	16	2			
29	Cu	2	8	18	1			
30	Zn	2	8	18	2			
31	Ga	2	8	18	3			
32	Ge	2	8	18	4			
33	As	2	8	18	5			
34	Se	2	8	18	6			
35	Br	2	8	18	7			
36	Kr	2	8	18	8			
37	Rb	2	8	18	8	1		
38	Sr	2	8	18	8	2		
39	Y	2	8	18	9	2		
40	Zr	2	8	18	10	2		
41	Nb	2	8	18	12	1		
42	Mo	2	8	18	13	1		
43	Tc	2	8	18	14	1		
44	Ru	2	8	18	15	1		
45	Rh	2	8	18	16	1		
46	Pd	2	8	18	18			
47	Ag	2	8	18	18	1		
48	Cd	2	8	18	18	2		
49	In	2	8	18	18	3		
50	Sn	2	8	18	18	4		
51	Sb	2	8	18	18	5		
52	Te	2	8	18	18	6		
53	J	2	8	18	18	7		
54	Xe	2	8	18	18	8		
55	Cs	2	8	18	18	8	1	
56	Ba	2	8	18	18	8	2	
57	La	2	8	18	18	9	2	
58	Ce	2	8	18	19	9	2	
59	Pr	2	8	18	20	9	2	
60	Nd	2	8	18	21	9	2	
61	Pm	2	8	18	22	9	2	
62	Sm	2	8	18	23	9	2	
63	Eu	2	8	18	24	9	2	
64	Gd	2	8	18	25	9	2	
65	Tb	2	8	18	26	9	2	
66	Dy	2	8	18	27	9	2	
67	Ho	2	8	18	28	9	2	
68	Er	2	8	18	29	9	2	
69	Tm	2	8	18	30	9	2	
70	Yb	2	8	18	31	9	2	
71	Lu	2	8	18	32	9	2	
72	Hf	2	8	18	32	10	2	
73	Ta	2	8	18	32	11	2	
74	W	2	8	18	32	12	2	
75	Re	2	8	18	32	13	2	
76	Os	2	8	18	32	14	2	
77	Ir	2	8	18	32	17		
78	Pt	2	8	18	32	17	1	
79	Au	2	8	18	32	18	1	
80	Hg	2	8	18	32	18	2	
81	Tl	2	8	18	32	18	3	
82	Pb	2	8	18	32	18	4	
83	Bi	2	8	18	32	18	5	
84	Po	2	8	18	32	18	6	
85	At	2	8	18	32	18	7	
86	Rn	2	8	18	32	18	8	
87	Fr	2	8	18	32	18	8	1
88	Ra	2	8	18	32	18	8	2
89	Ac	2	8	18	32	18	9	2
90	Th	2	8	18	32	18	10	2
91	Pa	2	8	18	32	18	11	2
92	U	2	8	18	32	18	12	2
93	Np	2	8	18	32	19	12	2
94	Pu	2	8	18	32	20	12	2
95	Am	2	8	18	32	24	9	2
96	Cm	2	8	18	32	25	9	2
97	Bk	2	8	18	32	26	9	2

a lack of saturation of the system causes chemical instability, which is manifested in a tendency to form large entities (molecules) grouping together with other atoms. By a suitable mutual distribution or by sharing of electrons of the electronic structure they change into stable systems, known in the rare gases. According to the way in which this arrangement of the electronic shells is achieved, the ionic (or heteropolar) bond and the covalent (or homeopolar) bond are known.

It is important to note, however, that no exact distinction is possible between these two types of bonds; it would be even more correct to consider the ionic type of bond and the covalent type of bond as extreme types which occur but rarely in pure forms and are more or less approached by the m lecules in all remaining cases, where characteristic features of both types manifest themselves at the same time.

The ionic type of bond is frequently encountered with such elements in which the number of electrons in the outer shell approaches the electronic configuration of the rare gases, therefore it can be encountered in the elements of the group of alkali- and alkaline-earth metals as well as in halogens and elements of the oxygen group. In the course of chemical reaction the atoms with an electron surplus above the octet yield these surplus electrons to those atoms which lack electrons for the completion of the octet. The atom which by the loss of electrons gained the stable electronic configuration of an inert gas, transforms itself into a positive ion (a cation) with a valence equal to the number of peripheral electrons lost. The other atom, having completed its outer shell to a closed sphere, changes into a negative ion (an anion) with a valence equal to the number of electrons gained for the completion of the octet.

Sodium with atomic number 11 has eleven protons in its nucleus. There are two electrons in the first closed electronic sphere, eight electrons in its second internal sphere, which is also complete, while in the third outer sphere there revolves the last solitary eleventh electron. Contrary to this, chlorine with atomic number 17 has two electrons in the first sphere, eight in the second and seven within the third; it needs only one electron for the completion of the octet in the last sphere. It will be readily appreciated that sodium and chlorine will react easily with formation of sodium chloride while the solitary electron from the third sodium sphere detaches itself and occupies the free place in the outer incomplete octet of the chlorine atom. Thus the chlorine of the resulting NaCl molecule has gained one electron and changed to a univalent Cl^- ion with a negative charge. The sodium atom has lost an electron and changed to a positive Na^+ ion. The reaction can be schematically written by the following equation:

$$Na. + .\dot{C}\dot{l}\cdot = Na^+ + (:\ddot{C}\ddot{l}:)^-$$

where points stand for the electrons in the outermost sphere. According to this equation as the electron passes from the sodium sphere to the chlorine sphere

both resulting ions gain the inert gas configurations (Na^+ having the neon and Cl^- the argon configuration).

Analogical molecular structure is possessed by other simple compounds such as potassium iodide, ammonium chloride, sodium hydroxide, barium nitrate, ammonium acetate and so on. In all these compounds there is a transfer of one or several electrons from one element to the other, positive and negative ions being thus formed, that are held together in a crystal by electrostatic attraction. A bond of this kind is no genuine chemical bond in the correct meaning of the term, but is just a result of Coulomb forces of attraction between opposite charges.

A significant feature of the ionic type of compounds is their comparatively high boiling point as well as their high freezing point and the fact that they conduct current as electrolytes. Their conductance in solid state is low, as the mobility of ions is hindered by electrostatic forces which in a crystal attain very high values because of the close proximity of oppositely charged particles. In molten state or in solutions where the electrostatic attraction between oppositely charged ions is substantially weakened either by the effect of thermal energy or as a result of the high dielectric constant of the solvent the conductance of ionic compounds is considerable. Under such conditions more or less independent ions are set free from compounds. By the effect of the outer electric field they rearrange their random motion and migrate toward oppositely charged poles of the outer electric field, in other words, they conduct the electric current. The process by which ions are formed or set free from a compound through the effect of thermal energy or of a suitable solvent is generally called electrolytic dissociation.

The other type of bond is the genuine chemical or covalent bond. Among the compounds of this type it is necessary to quote such chemicals as molecular hydrogen, nitrogen, water, ammonia, carbon dioxide, hydrogen chloride and many organic compounds. These compounds, unlike the type mentioned before, conduct little if any electric current, and both boiling and freezing points are comparatively low. The covalent bond is formed whenever one or several pairs of electrons are shared by a group of two or more atoms, whereby these latter achieve the stable configuration of the inert gases with the characteristic octet of electrons in the outer sphere (except helium with only two electrons).*)

These shared electrons are thus no more the exclusive property of one atom but are also a part of the electron system of the other atom. The formation of a fluorine molecule can thus be imagined in the following way: two atoms of this gas which lack one electron each to complete their outer spheres to a full octet satisfy each other by sharing a pair of electrons whereby the neon configuration is formed:

$$:\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}\cdot + \cdot\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}: = :\underset{\cdot\cdot}{\overset{\cdot\cdot}{F}} : \underset{\cdot\cdot}{\overset{\cdot\cdot}{F}}:$$

*) The rule mentioned, according to which the atoms are associating themselves to form a configuration with the electronic octet in the outermost sphere, has its exceptions, as systems are known with outer shells comprising ten or twelve electrons.

An atom that lacks more than one electron to complete its octet can achieve that completion by combining partially its electron orbital with those of several atoms. The formation of methane from elements can be, for example, expressed by the equation:

$$4\,H. + .\dot{\underset{\cdot}{C}}. = H : \underset{\cdot\cdot}{\overset{H}{\overset{\cdot\cdot}{C}}} : H$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\quad \ddot{H}$$

In this case of combination of elements each hydrogen atom contributes one electron for the formation of each of the covalent bonds, the other electrons being supplied by the carbon atom. In this way the outer carbon sphere is completed to the fully saturated sphere of the neon configuration, while the hydrogen sphere changes to the helium configuration.

In the cases above, each pair of electrons corresponds to a univalent bond. If a greater number of electrons is lacking, the incomplete spheres can attain the octet configuration by sharing two or three pairs of electrons. In a molecule of carbon dioxide the carbon is bonded with two oxygen atoms by two double valence bonds:

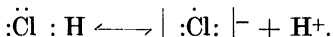
$$:\dot{O}: :C: :\ddot{O}:$$

The triple covalent bond with two atoms bonded by three pairs of electrons is known for instance in the case of nitrogen (N:::N:) or of acetylene (H : C:::C : H).

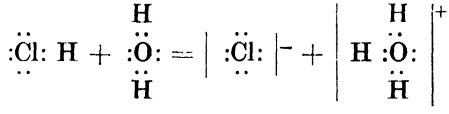
If all electrons of a covalent bond are shared equally by all atoms of a molecule (e . g . H_2, Cl_2, N_2 etc.), no atom can be considered "more positive" or "more negative" than the other. Such substances are said to be composed of nonpolar molecules. Where the compound is formed from atoms of different characters, the forces acting between the electrons and the respective atoms are generally not equal; the shared pair of electrons is then shifted more close to the atom by which it is more attracted. As a result of this shifting of electrons from one atom into the sphere of another the centers of the electrical gravity of electrons are no longer identical with the centers of electrical gravity of nuclei and the molecule becomes polarized. The covalent bond between different atoms of an unsymmetrical compound gives rise to a dipole which has the positive center of electrical gravity shifted beyond the negative center of electrical gravity. The cause of different affinity toward electrons of dissimilar atoms is to be found mainly in a different charge of that part of the atom which is inside the outer sphere of electrons. Examples of this type of compounds are water, ammonia, hydrogen cyanide, hydrogen fluoride, and sulphur dioxide.

Polar molecules develop an electrical field around themselves, therefore they are marked by the ability to attract either mutually themselves or other molecules with unsymmetrical electron structures. In this way we can explain the association of polar molecules (of water for instance) or the solvation of ions (hydration in case of water) caused by drawing in of the dipoles of water molecules into the electrical field of the ions (to be discussed further on).

The polarity of the chemical bonds can eventually be so strong, that one of the atoms practically does not share the common electrons. Such an extreme polar bond can be considered as a transitory stage between a perfect symmetrical covalent bond and the so called ionic bond caused by electrostatic forces between ions. An example of such compounds is hydrogen chloride the chlorine of which has a far greater affinity toward the electrons than the hydrogen, a fact manifested by the tendency of the compound to transform itself into a compound of ionic type composed of a chloride anion and a hydrogen cation.



Unless the necessary conditions for this transformation are given, the hydrogen remains bonded to the chlorine and the hydrogen chloride has the character of a typical covalent compound that conducts no current (in liquid state). The impulse to the separation of the hydrogen cation occurs on dissolving the hydrogen chloride in a suitable solvent, for instance water. According to the *Brönsted* conception the hydrogen chloride has the character of an acid the proton of which reacts with the base, in this case water, to form a hydroxonium ion $(H_3O)^+$ as in this form it is bonded more firmly than it was in the original acid.

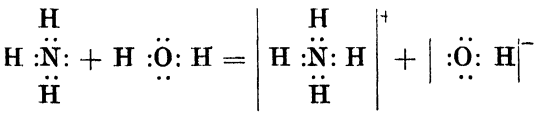


i. e.

$$HCl + H_2O = H_3O^+ + Cl^-$$

Water thus causes the electrolytic dissociation of the hydrogen chloride, which means the formation of a hydroxonium cation on one side and a chloride anion on the other side, so that the solution conducts electrical current. Ions of other acids are formed by analogical reaction with water.*)

Solutions of weak bases having polar bonds exert the same behavior as solutions of acids; ammonia can be given as an example. Ammonia in the liquid state is practically non-conducting, but in aqueous solutions it yields ions due to the following reaction:



*) The cation H^+ which according to former opinion is formed on dissociation of acids is incapable to exist independently in aqueous solutions; what was considered to be the hydrogen ion, is in fact the hydrated proton H_3O^+. As H^+ and H_3O^+ are mutually equivalent, the symbol H^+ can still be used lest we forget that this "hydrogen ion" has in fact the oxonium configuration which changes with the type of the solvent (for instance in solutions of ethylalcohole the ethyloxonium ion is formed $C_2H_5OH_2^+$).

i. e.

$$NH_3 + H_2O = NH_4^+ + OH^-.$$

According to the Brönsted theory ammonia behaves in this case like a base, capable to accept a proton from the acid (water) and to transform itself into a conjugated acid NH_4^+.

As this example shows, the decisive factor for the dissociation of polar compounds (HCl, NH_3) is first of all the formation of stable ions (H_3O^+, NH_4^+) the components of which are held together by chemical, covalent bonds. Because such compounds form ions only under the influence of a solvent, they are sometimes called potential electrolytes.

Unlike electrolytes of this type, the ionic compounds are called "true" electrolytes, because they already contain ions in their crystal lattice. In this case the solvent does not directly participate in the formation of ions, as in the case of the potential electrolytes, but only weakens the electrostatic attraction of existing ions to such a degree, that these do not associate again to form molecular aggregates. This reiterated association is hindered mainly by hydration in course of which the ions are envelopped by a protecting layer of water molecules, which separate them from the oppositely charged ions. So for instance the positively charged Cu^{++} ions in a solution of cupric chloride combine with the negative poles of polar molecules of water, whereby its attraction toward the Cl^- ions is considerably weakened.

B. ELECTRONIC AND ELECTROLYTIC CONDUCTORS

All substances can be divided from the point of view of their capability to conduct the electric current into conductors and non-conductors (insulators or dielectrics). The difference between these two groups is not always conspicuous as some substances can be denoted as poor conductors as well as imperfect insulators.

On the passage of electric current through the conductor the electricity moves from points with higher negative potential to points with lower negative potential. We must take into consideration the mechanism of this motion, which is not identical for all conductors but depends on their nature. So we have two classes of conductors, the electronic and the electrolytic conductors.

Electronic conductance is characteristic for the so called conductors of the first class, i. e. for metals (both in solid and fused state) and some metal oxydes, carbides, sulphides, phosphides and borides and it can be explained by assuming the existence of free electrons which act in solid matter as anions. Under the influence of the external electric field these easily movable electrons start an ordered motion while the atoms deprived of their electrons, which are in fact cations, take practically no part in the current conduction and, apart from their vibration within the mean equilibrium positions, remain practically immobile. The passage of the current does not manifest itself by a chemical change of the

conductor, but only by its warming up which is a result of the conversion of electric energy into thermal energy (in the case of some alloys the phenomenon of electrolysis has also been ascertained but at a negligible degree). Another characteristic property of the so called electronic conductors is the rise of their resistance with the temperature rise. This dependance is especially obvious within the range of very low temperatures, close to 3—4 Kelvin degrees, where the electrical resistance drops to such a low value that it is virtually of no hindrance to the passage of electrons (the so called superconductivity of metals).

Electrolytic conductance, a property of the so called conductors of the second class, is encountered mainly in the case of salts in dissolved, melted and solid state. Among these compounds are sulphates, halides, nitrates, silicates, also many oxides, hydroxides, sulphides and so on. The same group includes also the potential electrolytes, i. e. the substances from which ions are formed only in mutual reaction with a solvent (solutions of acids in basic solvents, solution of bases in acid solvents, further amines and different chlorine derivatives of organic compounds in liquid sulphur dioxide, nitro-compounds in liquid amines etc.). Finally also numerous colloidal solutions (such as proteins and soaps) conduct the current like electrolytes.

Unlike the electronic conductors the transfer of electricity is not mediated

Table 2. Conductances of electronic and electrolytic conductors

Substance	°C	$\varkappa(\Omega^{-1} \cdot cm^{-1})$
Electronic conductors		
Silver	18	625 000
Copper	18	584 000
Aluminium	18	356 000
Iron	18	100 000
Platinum	18	94 000
Nichrom	18	9 100
Graphite	18	750
Retort carbon	18	250
Saturated solution of sodium in liquid ammonia	—33,5	5 047
Electrolytic conductors		
Absolutely pure water	18	5×10^{-8}
Conductance water	18	$0{,}3-3{,}0 \times 10^{-6}$
20 p. c. solution of hydrochloric acid	18	0,76
30 p. c. solution of sulphuric acid	18	0,74
25 p. c. solution of sodium chloride	18	0,21
25 p. c. solution of calcium chloride	18	0,18
Fused calcium chloride	772	1,26
Fused silver nitrate	212	0,65
Fused sodium hydroxide	318	2,1
Solid α-silver iodide	150	1,3
Solid sodium chloride	700	7×10^{-5}

in this case by the "immaterial" free electrons but by positive and negative ions. Under the influence of the external electric field these mass particles with electric charges migrate to the oppositely charged electrodes which lead the current into the electrolyte. As the transfer of electricity in this case is connected with the transfer of mass to two different electrodes, the passage of electricity through a conductor of the second class causes also chemical changes in the composition of the electrolyte. Another characteristic property of the electrolytic conductors is the decrease of their electrical resistance with the increase of temperature.

Some substances manifest both electronic and electrolytic conductance at the same time. Among such conductors are some metal compounds such as solid silver sulphide, cuprous oxide, zinc oxide, cuprous chloride and similar substances. A special group includes solutions of alkali- and alkaline-earth metals in amines, namely in liquid ammonia, where appart from cations of metals and electrons bonded to the ammonia also free electrons are present at higher concentrations of solutions, whereby the conductance is considerably increased.

The difference between the specific conductances of electrolytic and of electronic conductors is clearly shown in Table 2. Also included are the values of conductances of absolutely pure water and of the so called conductance water, which is mostly used as a solvent for electrochemical measurements.

C. THE MECHANISM OF ELECTROLYTIC CONDUCTION OF ELECTRICITY

The mechanism of the passage of direct current through a conductor of the second class which is connected with a migration of ions and chemical reactions on electrodes can be most easily explained by an example. Let us imagine a vessel with two indifferent platinum electrodes A and C electrically connected to a source of direct current B and immersed into an aqueous solution of common salt in water (Fig. 1.).

Conventionally the direction of the current flow $B\ (+) \rightarrow A \rightarrow C \rightarrow B\ (-)$ is considered as positive. The direction of negative current which is identical with the movement of electrons is opposite, thus $B\ (-) \rightarrow C \rightarrow A \rightarrow B\ (+)$. From the theoretical point of view it is more correct to consider the direction of current according to the flow of electrons.

The electrons enter the solution from the source through the electrode C called the cathode, which is connected to the

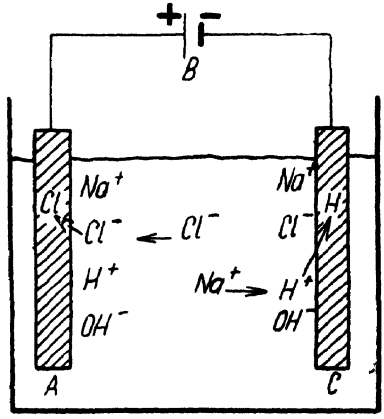


Fig. 1. Arrangement of an electrolyzer

negative pole of the source of current (thus the so called "positive" electricity leaves the solution at the electrode *C*). The electrode *A* connected to the positive pole of the source of current is called the anode. This is the electrode at which the electrons leave the solution and return to the source *B* or it is the point at which the "positive" electricity enters the solution.

The solution contains sodium and chloride ions besides a negligible number of hydrogen and hydroxyl ions which are the product of water dissociation. On the passage of current gaseous chlorine is liberated at the anode and gaseous hydrogen at the cathode; during this process the solution becomes alkaline in the proximity of the cathode, because sodium hydroxide is formed. The explanation of the process described is as follows: electrons *e* entering the solution from the cathode *C* are combining with hydrogen ions to form atomic hydrogen. Pairs of hydrogen atoms form hydrogen molecules on the electrode, which finally escape from the solution. Hydrogen ions are formed by the dissociation of water and after their discharge excess hydroxyl ions remain in the proximity of the electrode and cause an alkaline reaction of the solution. The total process at the cathode can then be expressed by the following equation:

$$2\,H_2O + 2\,e = H_2 + 2\,OH^-. \qquad \text{(I-1)}$$

At the moment, when, due to this reaction, two electrons are consumed at the cathode an equal number of electrons is set free at the other electrode (the anode) by two chloride ions yielding one elcctron each whereby they are transformed into two chlorine atoms. The electrons so set free then return through the outer conductor from the electrode to the source of the current, while nascent chlorine atoms combine in pairs to form molecules of gaseous chlorine which escape into the atmosphere. The anodic reaction can thus be written as:

$$2\,Cl^- = Cl_2 + 2\,e. \qquad \text{(I-2)}$$

We have learnt that the electrochemical reaction taking place at the cathode is connected with the acceptance of electrons. Such a process is generally called electrochemical reduction. Another example of the reduction is the cathodic deposition of metals (e. g. $Ag^+ + e = Ag$) or reduction of ions with higher valency to ions with lower valency (e. g. $Sn^{++++} + 2\,e = Sn^{++}$). The anodic process during which electrons are set free is called electrochemical oxidation. Such a process is for instance the oxidation of chloride ions to gaseous chlorine, anodic dissolution of metals, for instance $Cu = Cu^{++} + 2\,e$ or oxidation of ions with a lower valency to ions with a higher valency for instance $Fe^{++} = Fe^{+++} + e$. Until now we have followed the transfer of electricity at the electrodes. In the solution the current is transfered by anions and cations. The anions having a negative charge migrate under the influence of the electrical field which has arisen between the electrodes to the oppositely charged electrode, i. e. to the anode. The cations, charged negatively, migrate to the cathode. As, however, the transfer of positive electricity to the cathode

can be considered as a transfer of the negative electricity to the anode, the migration of cations is equivalent to the flow of electrons in the opposite direction. To sum up we can say that the migration can be considered as a movement of electrons through the solution from the cathode to the anode i. e. against the direction of the flow of "positive" electricity, according to which the positive and negative poles of the source of the current are conventionally distinguished.

According to what has been said above there are mainly Na^+ and Cl^- ions present in the considered solution of sodium chloride while H^+ and OH^- ions are present in far lesser concentration. On the passage of the current through the solution the chloride anions migrate toward the anode and discharge at it to form gaseous chlorine. Sodium ions migrate toward the cathode, but instead of them hydrogen ions are discharged at this electrode. Thus it can be seen that in some cases ions which migrate through the solution also take part in the reaction at the electrode while in other cases entirely different ions are being discharged at the electrode. This is due to the fact that with several kinds of ions of identical polarity in an electrolyte individual kinds of ions take part in the conduction of current in direct proportion to their respective specific conductances. At the electrodes, however, the ions which need the least electrical energy for their reduction or oxidation undergo an electrochemical reaction in preference. In the given case of electrolysis the current is transferred practically exclusively by sodium and chloride ions*) formed from sodium chloride because their specific conductance is much higher than that of the negligibly dissociated water. At the anode chloride ions are discharged in preference to hydroxyl ions as they require less energy for the discharge. At the cathode a preferential discharge of hydrogen ions takes place because the deposition of atomic hydrogen from its ionic state requires less energy than would be necessary for the deposition of sodium ions. Hydrogen evolution takes place in spite of the negligible concentration of hydrogen ions in a neutral or even alkaline solution. During the cathodic process hydroxyl ions remain in the proximity of the electrode after the deposition of hydrogen in accordance with the equation (I-1). These hydroxyl ions form a solution of sodium hydroxide with an equivalent number of sodium ions which have migrated into the proximity of the cathode.

Accordingly the passage of current through an electrolytic conductor is accompanied by a change in composition at different points of the electrolyte brought about by the migration and the chemical reaction of the ions at the electrodes. In such a process which is called electrolysis the electricity can enter the electrolyte, i. e. pass across the boundary between the conductors of the first and the second class only under simultaneous formation or discharge of ions at both electrodes. As no free charges can be formed in this case the same quantity of electricity must pass through both cathode and anode and the

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*) This is valid only for the beginning of the electrolysis as the concentration of the alkali hydroxide thus formed is still small; later on both alkali chloride and hydroxide take part in the conduction of current.

quantity of products on both electrodes must be mutually equivalent. The Faraday's law is an expression of this fact (see further).

D. THEORY OF ELECTROLYTES

In the chapter concerning elements of the molecular theory we have learnt which compounds can behave like electrolytes yielding ions when dissolved. In view of their capability to form ions i. e. according to their degree of electrolytic dissociation, we can distinguish between strong and weak electrolytes. The first group comprises, with few exceptions, all neutral salts and most inorganic acids and bases. The second group comprises in the first place nearly all organic acids and bases as well as some inorganic acids (H_2S, H_2CO_3, HCN, H_3BO_3, HClO etc.) and bases (aqueous solution of ammonia, zinc hydroxide, lead hydroxide etc.) and finally also some inorganic salts (such as $HgCl_2$, $Hg(CN)_2$, FeF_3 etc.).

The distinction between these two types of electrolytes is not sharply defined because electrolytes with a medium degree of dissociation are known (e. g. aqueous solutions of cyanoacetic acid, o-chlorbenzoic acid, o-nitrobenzoic acid, 3—5 di-nitrobenzoic acid etc.). As the number of such electrolytes is comparatively small, no special account will be taken of them. Analogically all nonaqueous solutions can be omitted as in technical electrochemistry water is exclusively used in the preparation of solutions of electrolytes.

Compared with solutions of nonelectrolytes the electrolytes manifest a greater elevation of the boiling point, greater depression of the melting point, a greater lowering of the vapour tension and a higher osmotic pressure than that which would correspond to their molecular weight.*)

These phenomena that were previously considered "anomalies" of the mentioned colligative properties of the solutions, have been dealt with by *Arrhenius* in his effort to explain such anomalies by his well known theory of electrolytic dissociation. According to this explanation the molecules of a dissolved electrolyte partly split to form smaller particles, i. e. ions, which from the thermodynamic point of view are as effective as the undissociated molecules themselves. As the number of particles of matter is thus greater, the manifestations of colligative properties are increased, compared to what they would be with an undissociated electrolyte.

According to the Arrhenius conception electrolytes dissociate in solutions to a certain degree that depends solely on the concentration at a given temperature. The dissociation is partial at finite concentration but it increases with increasing dilution and it becomes complete at infinite dilution. At a given temperature

*) The mentioned phenomena are among the remarkable properties of diluted solutions and are determined solely by the number of moles of substance dissolved in one unit of volume of the solution, not by the nature of that substance. Such properties, being functions of molar concentration only, are called colligative properties.

and a given concentration of the solution the remaining undissociated part of the electrolyte is in equilibrium with the ions formed and therefore the process of dissociation is subject to the law of mass action (Guldberg-Waage).

The theory of Arrhenius has proved its value with some minor supplements in explaining the behaviour of weak electrolytes, it failed, however, completely when applied to strong electrolytes. Success in the case of weak electrolytes can be explained by the fact that because of the comparatively small number of ions and because of the considerable distances between them, there is no substantial difference between ions and undissociated molecules as far as their individual behaviour is concerned. We may, therefore, assume that all these particles regardless of their nature play an equal part in the determination of the thermodynamic properties of the solution. The degree of dissociation has in this case a concrete meaning and individual weak electrolytes can be differentiated by their characteristic dissociation constants.

Unlike weak electrolytes, solutions of strong ones have a far higher specific conductance; the rise of the latter with rising concentration is also much more rapid. There is another difference: the anomalies ascertained in the colligative properties of strong electrolytes cannot be ascribed to partial dissociation of molecules to ions as in the case of weak electrolytes.

Also the so called degree of dissociation, determined from the colligative properties, does not agree with the result obtained from the measurement of the electrical conductance. Finally the law of chemical equilibrium, applicable to the dissociation of weak electrolytes, cannot be applied to the strong ones.

The reason why the Arrhenius theory failed in the case of strong electrolytes is this: with strong electrolytes there is a considerable number of ions present at all concentrations so that, even in rather diluted solutions, strong attractive electrostatic forces existing between the ions cannot be disregarded. Under such conditions the ions actually lose their independence owing to their interaction and their activities are suppressed to a certain degree by the vicinity of oppositely charged ions.

There is ample evidence that strong electrolytes are fully or almost fully dissociated in a solution. This is supported by the fact that already the crystal lattice of solid salts, which are typical representants of strong electrolytes, is built of ions, the distance between them merely becoming greater on dissolving. Molecules can exist only in considerably concentrated solutions, where they are formed secondarily by the association of ions released in the primary stage.

Taking into account the strong electrostatic charges of the ions one can hardly be surprised that with a greater number of the latter, mutual attraction between oppositely charged particles has a considerable influence on the degree of freedom of ions in the solution. It can also be conceived that electrostatic forces will limit the freedom of ions proportionally to the concentration of the solution and to the charge of the ions. It is only in infinitely diluted solutions that the interionic forces do not act and the colligative properties can be explained by a complete dissociation of the electrolyte according to the Arrhenius theory.

In all other solutions the so called degree of dissociation, as determined from the measurement of some colligative property, merely indicates the magnitude of interionic forces, it cannot, however, be taken as a measure of the quantity of dissociated and undissociated molecules of the solute. A complete theory of strong electrolytes, at least of their diluted solutions, has been developed by *Debye* and *Hückel*, this theory is the basis of modern electrochemistry.

In diluted solutions of strong electrolytes the valence type of a compound asserts itself to a much greater degree than its individual nature and so strong electrolytes are classified according to their charges as follows: An electrolyte splitting to two univalent ions (such as KCl) is denoted as uni-univalent or electrolyte of 1—1 type. An electrolyte yielding two univalent cations and one bivalent anion (such as Na_2SO_4) is called uni-bivalent or 1—2 type. Analogically bi-univalent (2—1), bi-bivalent (2—2) and uni-trivalent (1—3) and other types of electrolytes are known.

II. BASIC LAWS OF ELECTROCHEMISTRY
THE LAWS OF OHM AND FARADAY

Electric current is due to the existence of a difference of potentials at the ends of a conductor; this potential difference is called the voltage. According to Ohm's law the current I flowing through a given conductor is directly proportional to the voltage E and inversely proportional to the resistance R of that conductor

$$I = \frac{E}{R}. \tag{II-1}$$

The quantities I, E, and R are quoted in electrochemistry in so called international units. Among them there is the current unit one ampere (A or amp.), defined as a current that will deposit metallic silver from a solution of silver nitrate at a rate of 0,001118 grams per second. The unit of resistance is one ohm (Ω) which is the resistance of a column of mercury of uniform cross section at a temperature of 0 °C, 106.3 centimeters high and having a weight of 14.4521 grams (it has a cross section of 1 sq. millimeter).

Using Ohm's law the unit of voltage, called the volt (V), can be defined by the two precedent units as the potential difference required for a flow of current of one ampere through a conductor having a resistance of one ohm. In a closed electric circuit we can write the equation $E = IR$, E meaning the electromotive force of the source of current connected to the circuit. Ohm's law can also be applied, however, to a part of an electric circuit; then $E = IR$ stands for the voltage or potential difference across the given part of the conductor.

The product of I in amperes and of time t in seconds expresses the quantity of electricity q in coulombs passed through the conductor:

$$q = I\,t \tag{II-2}$$

One coulomb C or one ampere-second is a unit of quantity of electricity (electric charge) required to deposit 0,001118 grams of silver from a solution of silver nitrate regardless of the time during which the current passed through the electrolytic cell. This definition means that a current of one ampere represents a quantity of electricity equivalent to one coulomb per second.

Work W effected by current I on passage through resistance R in t seconds at a potential difference E is determined by Joule's law:

$$W = EIt = I^2Rt = Eq. \tag{II-3}$$

The unit of electrical work is called joule or watt-second (w-sec.) if E, I and R are quoted in V, A, and Ω units. In practice larger units are used, i. e. kilowatt-hours (kw-hr.), one kw-hr. being equal to $3{,}6 \times 10^6$ joule (w-sec.). Apart from units of mechanical energy, units of thermal energy are also em-

ployed for expressing quantities of electrical energy. Work quoted in joules can be converted to thermal units (calories) by using the equation:

$$1 \text{ joule} = 1 \text{ volt-coulomb} = 0{,}2389 \text{ cal} \tag{II-4}$$

Electric power designates the work effected by the current within a second; its unit is called watt (w) or kilowatt (kw), the latter being commonly used in engineering practice and equalling one thousand watts. Using equation (II-3) we obtain the following equation for the electric power N in watts:

$$N = \frac{W}{t} = EI = I^2R = \frac{Eq}{t}. \tag{II-5}$$

The resulting quantity in watts multiplied by 0,239 gives the power expressed in calories per second.

Faraday has developed the quantitative relations between quantity of electricity and its chemical effect and found a direct relation between the charges of ions and their respective valencies. According to his two laws, which can be united into one law, the number of chemical gram-equivalents of any substance formed or chemically changed at the electrodes is directly proportional to the quantity of electricity passed through the electrolytic cell. At the same time the electrochemical reaction of one gram-equivalent of any substance requires always the same quantity of electricity, namely $F = 96494$ C. This quantity of electricity has been called Faraday's charge (or one faraday) and designated by F. In common practice it is taken as $1\ F = 96500\ \text{C} = 26{,}8$ amp.-hr. (ampere-hours) which is the equivalent of a current of one ampere flowing for a period of 26 hours 48 minutes.

Faraday's law can be written as follows

$$m = \frac{A}{n} \cdot \frac{q}{F} = \frac{A}{nF} It = \alpha It, \tag{II-6}$$

where m designates the weight in grams of a substance which has taken part in the electrochemical reaction on passage of a quantity of current $q = It$ through the electrolytic cell. If A designates the atomic weight of the element or radical in question and n the number of electrons interchanged during the reaction (i. e. change of valency), then the quotient A/n designates the so called chemical equivalent. Considering for example the deposition of metallic iron from the state of bivalent ions ($Fe^{++} + 2e = Fe$) the chemical equivalent is given by one half of the atomic weight expressed in grams, i. e. 27,92 g. On the other hand let us take the example of bivalent iron being oxidized to trivalent ($Fe^{++} = Fe^{+++} + e$); in this case the gram-equivalent is equal to the atomic weight of iron expressed in grams, i. e. 55,84 g.

The symbol α in equation (II-6) which can be calculated from the formula

$$\alpha = \frac{A}{nF}, \tag{II-7}$$

stands for the electrochemical equivalent of the substance, i. e. the quantity of a substance in grams or milligrams deposited or consumed at the electrodes on passage of one coulomb through the electrolytic cell. Electrochemical equivalents of some substances are given in Table 3.

Table 3. Electrochemical equivalents

Element	Atomic weight A	Change of valence n	mg per amp.-sec.	Element	Atomic weight A	Change of valence n	mg per amp.-sec.
Ag	107,88	1	1,11793	H	1,0081	1	0,01044
Al	26,97	3	0,09316	Hg	200,61	2	1,03943
Au	197,2	3	0,68117			1	2,07886
		2	1,02176	J	126,92	7	0,18790
		1	2,04352			6	0,21921
Ba	137,36	2	0,71171			5	0,26305
Br	79,916	7	0,11831			4	0,32881
		6	0,13802			3	0,43841
		5	0,16563			2	0,65762
		4	0,20704			1	1,31523
		3	0,27605	K	39,096	1	0,40514
		2	0,41407	Mg	24,32	2	0,12601
		1	0,82815	Mn	54,93	7	0,08132
Ca	40,08	2	0,20767			6	0,09487
Cd	112,41	2	0,58244			5	0,11384
Cl	35,457	7	0,05249			4	0,14230
		6	0,06124			3	0,18974
		5	0,07349			2	0,28461
		4	0,09186			1	0,56921
		3	0,12248	Na	22,997	1	0,23831
		2	0,18372	Ni	58,69	3	0,20273
		1	0,36743			2	0,30409
Cr	52,01	6	0,08983			1	0,60819
		4	0,13474	O	16,00	2	0,08290
		3	0,17965	Pb	207,21	4	0,53681
		2	0,26948			2	1,07363
		1	0,53896	Pt	195,23	4	0,50578
Cu	63,57	2	0,32938			2	1,01155
		1	0,65876	Sn	118,70	4	0,30751
Fe	55,84	3	0,19288			2	0,61503
		2	0,28933	Zn	65,38	2	0,33876
		1	0,57865				

Faraday's law is a confirmation of our conceptions of electronic and electrolytic conductance. If the charge of an electron in coulombs equals $e = 1{,}60 \times \times 10^{-19}$ C and N the number of electrons received or set free during the electrochemical reaction of one chemical equivalent of a substance at the electrode, then the product of both

$$F = \mathrm{N}\, e \qquad \text{(II-8)}$$

denotes one Faraday's charge. As every ion of a univalent substance carries the unit charge e, then the symbol N must also be the number of atoms in one gram-atom or Avogadro's number ($N = 6{,}03 \times 10^{23}$). Faraday's charge ($F$) being determined by two constants, N and e, in accordance with the aforementioned equation, the product Ne is of necessity constant, too, thus independent on conditions of the electrolysis such as temperature, pressure, voltage, current, size of electrodes, concentration of electrolyte and so on. The equation (II-8) means further that Faraday's charge is a sum of elementary charges of $6{,}03 \times 10^{23}$ electrons taking part in the reaction of one chemical equivalent of a substance. One equivalent of positive ions lacks N electrons while one equivalent of negative ions has an exactly identical surplus of them. If a charge F passes through the solution $6{,}03 \times 10^{23}$ electrons are required for the reduction of the substance at the cathode while exactly the same number of electrons is set free at the anode as a result of some oxidation process. In the proper solution the same number of electrons is then transferred by migration of positive and negative ions to the corresponding electrodes.

Faraday's laws are classed among the most accurate laws of electrochemistry. Any departures from them are due to the fact that apart from the main process other, parallel processes can take place, requiring a certain quantity of current. When electrolysing a solution of copper sulphate under suitable conditions only copper will be deposited at the cathode; the yield of electrolysis then corresponds to a 100 p. c. current efficiency.

On the other hand when electrolyzing an aqueous solution of zinc sulphate we observe not only deposition of zinc at the cathode but also liberation of a certain amount of hydrogen so that the yield of zinc is less than would correspond to 100 p. c. current efficiency. When, however, the equivalents of deposited zinc and liberated hydrogen are added together, the current efficiency is 100 per cent. Nevertheless when speaking of current efficiency we always bear in mind a definite production, electrodeposition of zinc for instance, while the quantity of current required for the liberation of the hydrogen is considered to be a loss.

Current efficiency can also be reduced by chemical by-processes to which Faraday's law does not apply. Consequently such by-processes cannot be quantitatively explained by this law. On electrolyzing sodium sulphate, for instance, we obtain free sulphuric acid at the anode and sodium hydroxide at the cathode; both substances get mixed, however, due to diffusion and form the original sodium sulphate whereby the current efficiency proves lower. Some reduction of yields is also posible, due to mechanical losses such as evaporation of certain products of electrolysis, dispersion of them in the electrolyte or short circuits in the electrolyzer.

Current efficiency η_I is expressed by the ratio of the quantity of electricity q_t theoretically required for the electrochemical process according to Faraday's laws to the actual consumption of quantity of electricity q_s, expressed in percents

$$\eta_I = 100 \frac{q_t}{q_s}. \qquad \text{(II-9)}$$

As this value determines the economy of the electrochemical process we endeavour to create such conditions of electrolysis at which the unwanted by-processes are suppressed as much as possible. According to the degree of such suppression current efficiency varies in commercial practice from 30 to nearly 100 p. c.

Apparatuses called coulometers are used for the measurement of the quantity of electricity. These are in principle electrolytic cells in which a given electrochemical process is allowed to proceed under exactly defined conditions; it must be ascertained that the process in question proceeds in one direction only thus guaranteeing 100 p. c. current efficiency of electrolysis. From the amounts of products obtained which must be suitably determined, the quantity of electricity which passed through the cell can be calculated by applying Faraday's law.

One of the most accurate instrument for the measurement of quantities of electricity is the silver coulometer. A solution of purest silver nitrate in distilled water (20 to 40 parts $AgNO_3$ to 100 parts H_2O) is electrolyzed in a platinum crucible which serves as the cathode. An anode of pure silver rod is partly immersed into the solution and enclosed by a ceramic diaphragm so that mechanically separated anode slime cannot sink to the bottom of the crucible. Current density should not exceed 0,02 amp. per sq. cm. on the cathode and 0,2 amp. per sq. cm. on the anode. The level of liquid within the diaphragm should be somewhat lower than in the platinum crucible. When the electrolysis is finished the platinum crucible is washed with pure distilled water, dried and weighed. From the weight increase the quantity of electricity (in coulombs) passed through the solution is then calculated.

The copper coulometer is based on the same principle, but results of measurement are not quite so accurate.

This coulometer usually consists of a quadrangular glass vessel with two thick copper plates hanging as anodes along the longitudinal inside walls and one cathode of thin sheet copper, nearly wholly submerged in the electrolyte between them. The solution contains 125 to 150 grams of blue vitriol, 50 grams of concentrated sulphuric acid and 50 grams of alcohol in one litre of water The electrolysis is accomplished at a current density from 0,002 to 0,02 amp. per sq. cm. at the cathode; the solution is stirred by means of a stream of carbon dioxide in order to maintain exact working conditions. Again when electrolysis has ended, the cathode is washed with distilled water, dried and weighed.

If minute quantities of electricity are to be measured the electrolytic gas coulometer is recommended; in this case a 15 per cent solution of sodium hydroxide is used as electrolyte while the electrodes are of platinum or nickel. Both the hydrogen and the oxygen escaping from the closed electrolytic cell

are collected in an eudiometer and their volume is measured. This volume is then converted to S. T. P., i. e. to pressure of 760 mm Hg and temperature of 0 °C; the quantity of electricity is determined from this converted volume. This method has an advantage as current efficiency can be ascertained at any moment required without interrupting the electrolysis. If accurate results are to be obtained only hydrogen is collected as oxygen is comparatively soluble in water.

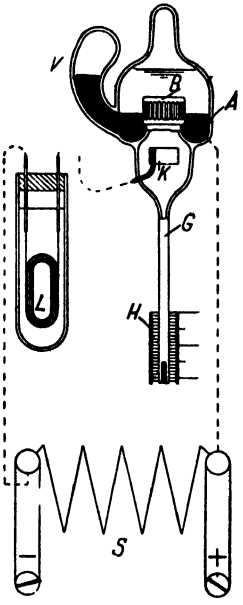


Fig. 2. The Stia coulometer.

For electrolysis lasting a long time or electrolysis requiring strong currents Hatfield's mercury coulometer (the so called Stia-counter) is suitable. The essential part of the instrument (Fig. 2.) consists of a closed glass vessel divided by a porous glass partition B into an upper compartment with a mercury anode A and a lower compartment with a carbon or irridium cathode K. The measured current flows through two circuit branches; one part flows through a shunt S, the rest is led into the coulometer proper through the metallic series resistance L, which compensates the change in conductance of the electrolyte caused by the heating effect of the current. Mercuric iodide in aqueous solution of potassium iodide is used as the electrolyte. On the passage of the current mercury dissolves at the anode and is deposited at the cathode, so that the composition of the electrolyte undergoes no change. The mercury deposited in the form of little droplets at the irridium electrode falls into a calibrated tube G provided with a scale H. The volume of mercury liberated by the electrochemical process is used for the determination of the quantity of electricity passed through the instrument. In the case the mercury rises to a point above the scale or if it has to be set to zero, the instrument will be inverted and the mercury alowed to flow back into the anode compartment.

Apart from the coulometers described, there are also instruments in which products of electrolyses are determined by titration. The iodine coulometer is based upon the anodic liberation of iodine from solutions of potassium iodide, the iodine being determined by titration with thiosulphate. Besides current efficiency also energy efficiency η_w is very important in technical practice. This is the ratio of theoretically required quantity of energy W_t to the quantity of energy W_s actually consumed for the electrochemical preparation of a given product (expressed as a percentage):

$$\eta_w = 100 \frac{W_t}{W_s}. \qquad \text{(II-10)}$$

On the substitution of W by its equivalent from the equation (II-3) we obtain

$$\eta_w = 100 \frac{q_t}{q_s} \cdot \frac{E_t}{E_s}, \tag{II-11}$$

where E_t means the voltage theoretically required and E_s the actual operating voltage of the electrolytic cell. The theoretical voltage E_t is identical with the decomposition voltage i. e. the minimum potential difference at the terminals of the electrolyzer necessary to start the electrochemical process. This will be discussed later in greater detail. In an electrolyzer under current load the necessary voltage E_s is of course higher, because it also must overcome the resistance of the electrolyte and other hindrances opposing the passage of a current of required strength through the electrolytic bath.

Calling ratio E_t/E_s the voltage efficiency η_E and taking into account also the equation (II-9), we can give to the equation (II-11) the following simple form:

$$\eta_w = \eta_I \eta_E, \tag{II-12}$$

This means that energy efficiency is a product of current efficiency and voltage efficiency.

III. ELECTROLYTICAL CONDUCTANCE

When current I passes through an electrolyte it is opposed by resistance R which must be overcome by voltage E according to Ohm's law:

$$E = IR \tag{III-1}$$

The magnitude of this resistance depends on the nature, the dimensions and the temperature of the electrolyte. Its value at a given temperature can be calculated from the specific resistance of the electrolyte ϱ (i.e. from the resistance

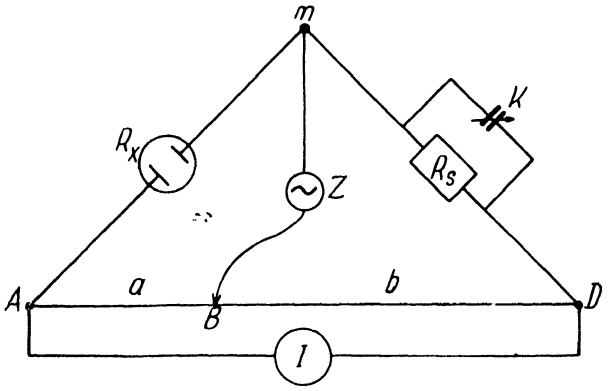


Fig. 3. Wheatstone bridge for measurement of resistances.

in ohms of a cube of solution having sides 1 centimeter long), from the length of the conductor l (distance between electrodes in centimeters) and from the cross section of the conductor q (effective area of electrodes in sq. cm) follows the equation

$$R = \varrho \frac{l}{q}, \tag{III-2}$$

The dimensions of the specific resistance is Ω . cm. The reciprocal value of the specific resistance is called specific conductance $\varkappa$ and is designated by the symbol mho; its dimension is Ω^{-1} . cm^{-1}. On substituting this quantity into the above equation (III-1), the following equation results:

$$I = \frac{E}{R} = E \frac{q}{\varrho l} = E \varkappa \frac{q}{l}, \tag{III-3}$$

In case $q = 1$ sq. cm, $l = 1$ cm and $E = 1$V, the specific conductance equals the current I' that passes through the electrolyte:

$$I' = \varkappa. \tag{III-4}$$

Specific conductance (or conductivity) is measured by the Wheatstone bridge methode. The bridge is connected with a source of alternating current of a frequency of about 1000 cycles per second generated in an induction coil (inductor) or in an oscillator composed of thermionic valves and electromagnetic oscillatory circuits. Direct current must not be used for measurement because electrolysis of the solution would occur and cause a change in its composition near the electrodes; apart from this, gas bubbles liberated on the electrodes during the process would increase the resistance of the electrolyte and give rise to a polarization potential which would weaken the current passing through the measuring vessel. Assuming that the alternating current has a symmetrical

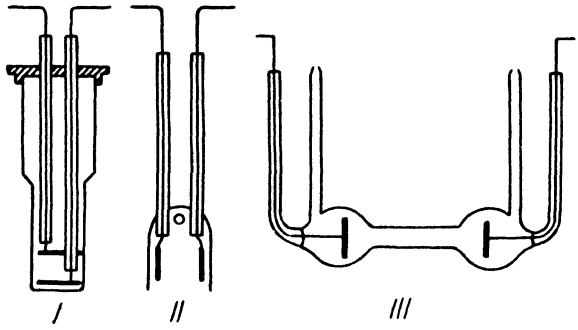


Fig. 4. Cells for measurement of conductance of solutions.

sinusoidal course, each single wave compensates the electrochemical effects of the preceding one, so that the difficulties referred to above are no longer encountered.

Arrangement of the apparatus is illustrated in Fig. 3, where R_x denotes a small vessel containing the solution the resistance of which is to be measured, R_s a known variable resistance up to 10 000 or 20 000 ohms, Z a source of alternating current, and I a current detector (such as earphones or a magnetic eye, the latter being a small Brown's tube). The source of alternating current is connected to point m on one side and to sliding contact B on the other side; contact B is moved along the measuring resistance wire AD with an attached metering scale or wound round an ebonite drum. On measuring one has to slide the contact B on the measuring wire till no detectable current is passing through the indicator. On this condition the ohmic resistance across single branches of the bridge satisfies the equation

$$\frac{R_x}{R_s} = \frac{a}{b}, \qquad \text{(III-5)}$$

from which resistance R_x can be determined provided resistance R_s is known and the ratio of the length of both sections of the measuring wire, i. e. a/b is

measured. In the case of electrolytes having minute conductance variable condenser K is used in addition; it is connected parallel to resistance R_s to compensate the capacity of conductance cell R_x which makes the ascertaining of the balance more difficult. Modern sets have a series of different resistances instead of the measuring wire; these resistances are connected in series according to the value of the resistance measured. The accurate compensation to zero then occurs within very narrow resistance limits.

The conductance cells different in shape which are illustrated in Fig. 4. are of glass or quartz; two exactly parallel electrodes made of thick platinum sheet (in order to keep constant their mutual position) are dipped into the cells. To suppress the polarization phenomena the electrodes are coated with platinum black. The current is fed through glass tubes filled with mercury; the connections of the electrodes are sealed in the glass at the bottom of the tubes while at the top lead-in wires are immersed in the mercury for connection with the terminals of the measuring instruments.

Prior to measurement the measuring cell must be calibrated using a solution of known specific conductance (0,02 molar solution of potassium chloride is used as a rule) whereby the so called cell constant $C = l/q$ is determined.

In case the resistance of the cell filled with 0,02 molar solution of potassium chloride with a specific conductance $\varkappa' = 0{,}002768$ mho at 25 °C is designated by R', then the cell constant will be calculated from Ohm's law

$$R' = \rho' \frac{l}{q} = \frac{C}{\varkappa'} = \frac{C}{0{,}002768},$$

thus

$$C = 0{,}002\,768\ R'.$$

The specific conductance of the solution to be measured $\varkappa$ is then determined from the value of its resistance R according to the formula

$$\varkappa = \frac{C}{R}. \qquad \text{(III-6)}$$

When preparing the solutions the conductance of which is to be measured, water of the maximum possible purity is used. Absolutely pure water has a specific conductance of about 5×10^{-8} mho. As measurement then has to be undertaken in the absence of air, such water is used for the most accurate work only. So called conductance water meets the requirements of general practice; it is prepared by a redistillation of normal distilled water with a small addition of permanganate and sodium hydroxide in a hard glass apparatus. Its higher conductance of some 0,3 to $3{,}0 \times 10^{-6}$ mho is mainly due to dissolved carbon dioxide.

For accurate measurements of solutions of salts, which are not hydrolysed to a greater degree, the conductivity of water used in preparation has to be

deducted (water correction) in order to determine the conductance due to the salt only.

$$\varkappa_{\text{salt}} = \varkappa_{\text{solution}} - \varkappa_{\text{water}}.$$

In case of acid solution this water correction is omitted, as the present acid suppresses to a sufficient degree the dissociation of carbonic acid which is the cause of the "conductivity" of the conductance water. On measuring the conductivity of alkaline solutions the correction may also be neglected.

Specific conductance, apart from other factors, also depends on concentration, i. e. on the amount of substance dissolved in one millilitre (ml) of the solution. To exclude this varying influence the conception of equivalent conductance Λ has been introduced. The quantity Λ represents the conductance of that volume of the solution which contains exactly one gram-equivalent of the substance dissolved and is placed between two parallel electrodes of sufficient size which are set exactly 1 cm apart. According to this definition the equivalent conductance does not depend on the amount of substance in the solution but solely on its state (i. e. upon the degree of dissociation of the electrolyte and the magnitude of interionic attraction forces) which is determined by the concentration of the solution. (If this state did not change on dilution the equivalent conductance would be equal at all concentrations). If φ is the volume of solution (in millilitres) containing 1 gram-equivalent of the substance dissolved and c_e the concentration expressed by the number of gram-equivalents of the substance in one litre the equivalent conductance will be calculated from the specific conductance $\varkappa$ using the following equations:

$$\Lambda = \varphi\varkappa, \tag{III-7}$$

$$\varphi = \frac{1000}{c_e}. \tag{III-8}$$

$$\Lambda = \frac{1000\varkappa}{c_e}. \tag{III-9}$$

On substitution of these values into equation (III-3) we obtain

$$I = E\frac{\Lambda}{\varphi}\frac{q}{l} = E\frac{\Lambda c_e}{1000}\frac{q}{l}. \tag{III-10}$$

If $E = 1$ V, $q = \varphi$ sq. cm, $l = 1$ cm, and $C_e = 1000/\varphi$ gram-equivalents per liter, the equivalent conductance equals the current I'' passing through the electrolyte:

$$I'' = \Lambda. \tag{III-11}$$

The equivalent conductance thus represents the quantity of electrical charge transferred per unit of time by ions present in a volume of solution of a given concentration containing one gram-equivalent of the electrolyte placed between two electrodes set 1 cm apart and at unit potential difference across them.

Apart from the equivalent conductance another quantity is used, namely the molar conductance μ; under this we understand the conductance of that volume of solution which contains one mole of dissolved substance and is placed between two parallel electrodes of sufficient size and set 1 cm apart. If one gram-molecule of a substance corresponds to $n = \nu z$ gram-equivalents of the ions (z being the number of charges of an ion and ν the number anions or cations formed by the dissociation of the molecule) then the following relation can be found between equivalent and molar conductances:

$$\mu = \nu z \Lambda. \qquad \text{(III-12)}$$

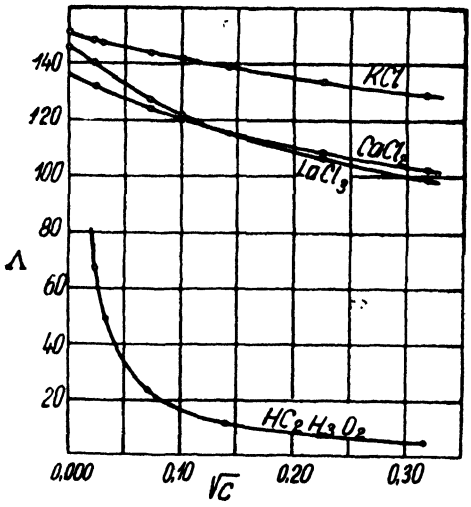


Fig. 5. Dependence of equivalent conductance Λ on concentration $\sqrt{c}$.

It will be seen from the above equation that in the case of electrolytes composed of two univalent ions there is no difference between molar and equivalent conductances. In case of electrolytes with bivalent ions the molar conductance is double of the equivalent conductance, with trivalent ions treble and so on.

Both specific and equivalent conductances depend to a great extent on the concentration of the solution as well as on the circumstance whether the solution in question contains a weak or a strong electrolyte.

The specific conductance of strong electrolytes increases up to concentrations of some tenth of gram-equivalents per litre, in almost direct proportion to the increasing concentration. The conductance of solution of weak electrolytes is in general less and its increase with rising concentrations much slower. Should the concentration rise from 0.001 N to 0.05 N then at 25° C the specific conductance of hydrochlorid acid, for instance, would increase from 4.21×10^{-4} to 199.5×10^{-4} mho, while for a solution of acetic acid such an increase would be from 0.49×10^{-4} to 3.70×10^{-4} mho only. In both previous cases the increase in specific conductance is due to the presence of more ions in one millilitre of the solution. While in strong electrolytes the number of ions in one millilitre (ml) of solution increases almost in direct proportion to the concentration, the increase in the number of ions in weak electrolytes is much slighter as the degree of dissociation decreases with increasing concentration.

Unlike specific conductance the equivalent conductance of both strong and weak electrolytes drops with increasing concentration and increases with decreasing concentration up to a certain limit value Λ° (see Table 4 and Fig. 5).

Table 4. Equivalent conductances of aqueous solutions of electrolytes at 25 °C

Electrolyte	Concentration in equ. per litre										
	0,0000	0,0005	0,001	0,005	0,01	0,02	0,05	0,10	0,20	0,50	1.00
NaCl	126,45	124,50	123,74	120,65	118,51	115,76	111,06	106,76	101.6	93,3	—
KCl	149,86	147,81	146,95	143,55	141,27	138,34	133,37	128,95	123,9	117,2	111.9
HCl	426,16	422,74	421,36	415,80	412.00	407,24	399,09	391,32	379,6	359,2	332,8
$AgNO_3$	133,36	131,36	130,51	127,20	124,76	121,41	115,24	109,14	101,8	—	—
NaOH	248	246	245	240	237	233	227	221	—	—	—
$^1/_2H_2SO_4$	429,6	413.1	399,5	364,9	336,4	308,0	272,6	250,8	234,3	222.5	—
$^1/_2Na_2SO_4$	129,9	125,74	124,15	117,15	112,41	106,78	97,75	89,98	81,5	—	—
$^1/_2BaCl_2$	139,98	135,96	134.34	128,02	123,94	119,09	111,48	105,19	98,6	88,8	80,5
$^1/_2CuSO_4$	—	—	115,2	97,5	83,3	72,2	58,8	50.5	43,5	35,1	29,3
$^1/_4K_4Fe(CN)_6$	184	—	167,24	146,09	134,83	122,82	107,7	97.87	—	—	—
NH_4OH	271,4	17	34	16	11,3	8,0	5,1	3,6	—	—	—

The latter quantity, although called the equivalent conductance at infinite dilution, does not mean the conductance of a pure solvent but the conductance of a gram-equivalent of substance in such a diluted solution in which the ions no longer affect one another. As will be seen from Fig. 5. the dependence of equivalent conductance on concentration of the solution is fundamentally different for strong electrolytes and for weak ones. Equivalent conductance of strong electrolytes rises slightly with increasing dilution and approaches the limit value Λ° already at a concentrations of 0.001 to 0.0001 N. Therefore in choosing a suitable scale for the concentration we are able to determine the limit value Λ° by extrapolation of ascertained values to zero concentration (see equation (III-14) further on).

On the other hand the equivalent conductance of weak electrolytes rises much steeper on dilution yet it doesn't nearly attain its limit value Λ° at concentrations mentioned in the previous case. As the measurement of the conductance at still higher dilution is extremely inaccurate due to high resistances of the solution, the same method of extrapolation as used with the strong electrolytes is unsuitable for determination of Λ° of weak electrolytes. In such cases we resort to the Kohlrausch law of independent migration of ions, to be discussed further on.

The dependence of the equivalent conductance on the concentration of the solution is due to the dissociation of the electrolyte on one hand and to mutual interaction of ions on the other. The first factor is of primary importance in the case of weak electrolytes. As the degree of dissociation increases with increasing dilution, the decrease of specific conductance $\varkappa$ is slower than would correspond to the decrease of the analytical concentration c_e. Therefore equivalent conductance rises with decreasing concentration of the solution as will be seen from the equation $\Lambda = 1000\,\varkappa/c_e$. The other factor, namely mutual interaction of ions, manifests itself at higher concentrations of solutions only.

Contrary to weak electrolytes, even the less diluted solutions of strong

electrolytes contain sufficient number of ions, because they are completely dissociated. The effect of forces of attraction between opposite charges of ions retards the free motion of the latter. The conductance of the solution is thereby reduced below the value of the conductance of a solution with entirely free ions.

By the assumption of the idea of the ionic atmosphere Debye and his coworkers succeeded to express mathematically the influence of electrostatic forces upon the mobility of ions. As will be discussed later, Debye's theory is, that every ion is surrounded by a group of ions in the manner of a spherical atmosphere, the resultant charge of which is equal to that of the central ion, but of an opposite sign. In a stationary state the ionic atmosphere is perfectly symmetrical, thus the intensity of the electrical field between the atmosphere and the central ion is uniform in all directions. As soon, however, as the electrolyte is exposed to the action of an external electrical field, the ions are brought into motion and migrate to the electrode possessing the opposite charge respectively. The mobility of individual ions is, however, less than it would be in the case of mutually independent particles of the same size exposed to the action of the field of force of the same intensity. This is so, because two forces, arising simultaneously on the passage of current through the electrolyte, hinder the motion of electrically charged ions.

One of these forces is caused by the so called *relaxation effect*. In the process of ionic migration each moving central ion has constantly to built up its new ionic atmosphere in the direction of its movement while the old one gradually decays. Since, however, the formation and the destruction of the ionic atmosphere does not occur instantaneously but requires a finite time of "relaxation", the ionic atmosphere does not keep pace with the migrating ion and lags behind it with a certain retardation. The result of this will be an excess of oppositely charged ions behind the central ion which will exercise a retarding effect on its motion. This influence on the speed of ions is also known as the "asymmetry" effect, since it is caused by the lack of central symmetry in the electrical atmosphere surrounding the central ion.

The second retarding factor arises from the tendency of the applied external electromotive force to move the ionic atmosphere with its solvation sheath in the direction opposite to that of the central ion. These counter-currents of the solvent act in the same way as an increased viscosity of the medium, i. e. they make it more difficult for the ions to travel through the solution and slow them down. This additional retarding influence is called the "*electrophoretic*" *effect*, since it is analogous to the resistance opposing the movement of a colloidal particle in an electrical field. The greater the charge density of the ionic atmosphere, i. e. the higher the concentration of the solution, the stronger the influence of both retarding effects. On the other hand in an infinitely diluted solution the effect of interionic forces disappears.

Debye, Hückel and Onsager beginning with these conceptions found an interdependence of the equivalent conductance Λ of a given solution, the con-

centration c_e (in g-equ./litre) of the solution and the temperature. The corresponding equation can be written in its general form:

$$\Lambda = \Lambda^\circ - \Lambda_I - \Lambda_{II} = \Lambda^\circ - a\Lambda^\circ \sqrt{c_e} - b \sqrt{c_e} \qquad \text{(III-13)}$$

where Λ_I stands for the lowering of equivalent conductance Λ° at infinite dilution caused by the relaxation effect and Λ_{II} for the decrease in conductance due to the electrophoretic forces; a and b are constants the value of which depends on the type of electrolyte, type of solvent and temperature. In the case of aqueous solutions of uni-univalent electrolytes and at a temperature of 25 °C the general equation can be written in the following form:

$$\Lambda = \Lambda^\circ - (60.2 + 0.229\,\Lambda^\circ) \sqrt{c_e} = \Lambda^\circ - k \sqrt{c_e}. \qquad \text{(III-14)}$$

Λ° being a constant for a given electrolyte, the term in brackets is constant too and the above equation is in fact an equation of a straight line, if the values of $\sqrt{c_e}$ are marked as abscissae and the values of Λ as ordinates. If a diagram is constructed from values found experimentally the connecting line of the individual points will be almost a straight line. By extrapolation to the concentration of $c_e = 0$ the point of intersection of the straight line with the ordinate axis can be found, the ordinate of which represents the value of Λ_o. (see Fig. 5). Some values of Λ° obtained in this way for some strong electrolytes are given in the first column of Table 4 ($c_e = 0$).

Up to concentration of 2×10^{-3} gram-equivalents per litre there is a satisfactory agreement between the results calculated from the Debye-Hückel-Onsager equation and the actual values of conductance of uni-univalent electrolytes. The validity of this equation has been verified even for uni-bivalent electrolytes, while for bi-bivalent electrolytes there are greater deviations to be observed.

The equivalent (as well as specific) conductance of electrolytes increases with rising temperature as a result of greater mobility of the ions. This dependence can be expressed by the equation:

$$\Lambda^\circ_{(t)} = \Lambda^\circ_{(25°C)} [1 + \beta\,(t - 25)] \qquad \text{(III-15)}$$

where $\Lambda^\circ_{(t)}$ and $\Lambda^\circ_{(25°C)}$ stand for equivalent conductances at infinite dilutions and at temperatures of $t°$ or 25 °C respectively, and β is the temperature coefficient of the given electrolyte, depending mainly on the viscosity of the solvent (β equals 0.022 to 0.025 for salts and 0.016 to 0.019 for acids and bases). The increase of conductance with a rising temperature is due mainly to a lowering of viscosity of the solvent and partly also to a lesser solvation of ions.

The conductance of electrolytes is caused by ions which are brought into motion by the effect of the electrical field. The velocity of the ions increases from the first moment the current is led into the solution but it attains a constant value as soon as the actuating force equals the resistance encountered by the ions on their respective path (viscosity of the medium and electrostatic

forces acting in opposite direction). The resultant velocity of ions in centimeter per second (cm./sec.) depends on their nature, the concentration of the solution, the temperature and the potential gradient between the electrodes. This velocity is usually converted to the potential gradient of 1 V across 1 centimeter of the path and expressed in units cm/sec. (V/cm). This quantity is called the absolute velocity or the ionic mobility.

The relation between the conductance of a solution and the velocity of ions can be arived at by the following reasoning: Let us consider a cell with two electrodes set exactly 1 cm apart and of sufficient areas to contain a volume φ of a solution, containing 1 gram-equivalent of the electrolyte, between them. If the potential difference between the two electrodes equals 1 V the current passing through the system equals the equivalent conductance (see equation III-11).

The electrolyte $A_{\nu+}\,B_{\nu-}$ is dissociated into ions according to equation:

$$A_{\nu+}\,B_{\nu-} = \nu_+ A^{z+} + \nu_- B^{z-} \tag{III-16}$$

where z_+ and z_- indicate the number of charges of the ions, and ν_+ and ν_- the number of gram-ions arising from one mole of the compound $A_{\nu+}\,B_{\nu-}$. In view of the electroneutrality we can write

$$z_+\nu_+ = z_-\nu_-. \tag{III-17}$$

Both anions and cations take part in the transport of electricity so that the conductance of an electrolyte equals the sum of conductances of both species of ions. The conductance of each ion depends on the magnitude of elementary ionic charge e, the quantity of ions within the given volume of the solution (n_+, n_-), their respective valencies (z_+, z_-) and absolute velocities (v_+, v_-) at a potential gradient of 1 V/cm. The contribution of cations A^{z+} to the total conductance of the solution is thus given by the product $(en_+z_+v_+)$ and the contribution of anions B^{z-} by the product $(en_-z_-v_-)$. The summary equivalent conductance of the solution may then be expressed by following sum:

$$I'' = \Lambda = en_-z_-v_- + en_+z_+v_+. \tag{III-18}$$

If α is the degree of dissociation of the electrolyte then from one mole of substance dissolved, $\alpha\nu_+\mathrm{N}$ positive ions and $\alpha\nu_-\,\mathrm{N}$ negative ions are formed; N stands for Avogadro's number (i. e. the number of atoms in a gram-atom or of molecules in a gram-molecule $\mathrm{N} = 6.03 \cdot 10^{23}$). In the given case, however, there is only 1 gram-equivalent contained in the volume considered, i. e. $1/z_+\nu_+ = 1/z_-\nu_-$ mole of the electrolyte so that on dissociation of the latter only $n_+ = \alpha\nu_+\mathrm{N}/z_+\nu_+ = \alpha\mathrm{N}/z_+$ positive ions and $n_- = \alpha\nu_-\,\mathrm{N}/z_-\nu_- = \alpha\,\mathrm{N}/z_-$ negative ions are liberated. Since the product of Avogadro's number with the elementary charge of an electron equals one Faraday's charge $F = \mathrm{N}e$ (see equation II-8) the equation (III-18) can be converted into following form:

$$\Lambda = \alpha e\mathrm{N}\,(v_+ + v_-) = \alpha F\,(v_+ + v_-). \tag{III-19}$$

If in this equation we substitute:

$$F\alpha v_+ = \lambda_+ \qquad \text{(III-20a)}$$

$$F\alpha v_- = \lambda_- \qquad \text{(III-20b)}$$

we finally obtain:

$$\Lambda = \lambda_+ + \lambda_-. \qquad \text{(III-21)}$$

This important equation expresses the fact that the conductance Λ of a solution is an additive property and that it equals the sum of the cation conductance λ_+ and of the anion conductance λ_-. When applying the equation (III-21) we must, however, bear in mind that the ionic conductances λ_+ and λ_- (as well as the velocities v_+ and v_-) are dependent on concentrations, so that in every particular case their respective values have to agree with the composition of the solution in question. Apart from this it must be remembered that the mutual electrostatic attractions of ions vary at definite concentrations according to the nature of the electrolyte so that the equation (III-21) does not always yield quite accurate results for arbitrary combinations of cations and anions.

The last mentioned reservation is not valid for infinitely diluted solutions in which the oppositely charged ions no longer affect one another so that every ion transfers electricity as though there were no other ions. Under such condition the equation (III-21) can be written in the form

$$\Lambda^\circ = \lambda_+^\circ + \lambda_-^\circ \qquad \text{(III-22)}$$

which is a mathematical expression of the Kohlrausch law of the independent migration of ions; in this equation Λ° stands for the equivalent conductance of the solution at infinite dilution and λ°_+ as well as λ°_- for the corresponding ionic conductances of cations and anions. The values of ionic conductances of some ions in the condition of infinite dilution at 25°C are given in Table 5. Availing ourselves of values taken from this table we can calculate Λ° of both strong

Table 5. Equivalent ionic conductances at infinite dilution (25 °C)

Cations	λ°_+	Anions	λ°_-
H^+	349,82	OH^-	198
Tl^+	74,7	$\frac{1}{4}Fe(CN)_6^{----}$	110,5
K^+	73,52	$\frac{1}{3}Fe(CN)_6^{---}$	101,0
NH_4^+	73,4	$\frac{1}{2}SO_4^{--}$	79,8
$\frac{1}{2}Ba^{++}$	63,64	Br^-	78,4
Ag^+	61,92	J^-	76,8
$\frac{1}{2}Ca^{++}$	59,50	Cl^-	76,34
$\frac{1}{2}Sr^{++}$	59,46	NO_3^-	71,44
$\frac{1}{2}Mg^{++}$	53,06	ClO_4^-	68,0
Na^+	50,11	HCO_3^-	44,48
Li^+	38,11	CH_3COO^-	40,9

and weak electrolytes. So for instance the equivalent conductance of acetic acid, a weak electrolyte, equals:

$$\lambda^\circ_{(HAc)} = \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-} = 349.8 + 40.9 = 390.7 \text{ mho.}$$

Analogically Λ° of a strong electrolyte, sodium chloride for example, will be calculated as follows:

$$\Lambda^\circ_{(Nacl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Cl^-} = 50.11 + 76.34 = 126.45 \text{ mho.}$$

The value of Λ° of a given electrolyte can also be determined using equivalent conductances of other electrolytes with either identical cation or anion. So for instance the equivalent conductance of acetic acid can be determined if we add Λ° of hydrochloric acid and Λ° of sodium acetate and substract Λ° of sodium chloride:

$$\Lambda^\circ_{(NaAc)} + \Lambda^\circ_{(HCl)} - \Lambda^\circ_{(NaCl)} = \lambda^\circ_{Na^+} + \lambda^\circ_{Ac^-} + \lambda^\circ_{H^+} + \lambda^\circ_{Cl^-} - \lambda^\circ_{Na^+} - \lambda^\circ_{Cl^-} =$$
$$= \lambda^\circ_{H^+} + \lambda^\circ_{Ac^-} = \Lambda^\circ_{(HAc)}.$$

From the known values λ°_+ and λ°_- the corresponding velocities of ions v°_+ and v°_- can be finally calculated on substituting $\alpha = 1$ (valid at infinite dilution) in equations (III-19 and III-20)

$$\Lambda^\circ = F\,(v^\circ_+ + v^\circ_-), \qquad \text{(III-23)}$$

$$v^\circ_+ = \frac{\lambda^\circ_+}{F} \qquad \text{(III-24a)}$$

$$v^\circ_- = \frac{\lambda^\circ_-}{F}. \qquad \text{(III-24b)}$$

Numerical values of absolute velocities of some ions at infinite dilutions are contained in Table 6.

Table 6. Absolute velocities of ions at infinite dilutions in cm/sec . (V/cm) (at 25 °C)

Cations	v°_+	Anions	v°_-
H^+	0,003620	HCO_3^-	0,002050
Tl^+	0,000774	$Fe(CN)_6^{----}$	0,001140
K^+	0,000762	$Fe(CN)_6^{---}$	0,001040
NH_4^+	0,000760	SO_4^{--}	0,000827
Ba^{++}	0,000659	Br^-	0,000812
Ag^+	0,000642	J^-	0,000796
Ca^{++}	0,000616	Cl^-	0,000791
Sr^{++}	0,000616	NO_3^-	0,000740
Mg^{++}	0,000550	ClO_4^-	0,000705
Na^+	0,000520	HCO_3^-	0,000461
Li^+	0,000388	CH_3COO^-	0,000424

According to experience with the motion of particles in liquids it can be anticipated that an ion having a small diameter would have a greater mobility than a large one. The opposite is true in the case of alkali metal and halogen ions. This can be explained by the various degree of their respective hydration. The smaller the diameter of an ion the stronger the electrical field around it which attracts a certain number of molecules of a polar solvent (such as water). A shell of solvent dipoles is thus formed around the ion firmly bound to it. The solvated ions (hydrated in the case of an aqueous solution) then migrate as indivisible units and their motion under the effect of the electrical field is slower than that of simple ions of a smaller diameter.

The abnormally great mobility of ions H^+ and OH^- is not due to their small diameter as the H^+ ion actually exists as the hydroxonium ion H_3O^+ that is about as large as Na^+ ion. The OH^- ion is approximately the size of the F^- ion. The mentioned ions are transferred more quickly than others as their normal migration is accompanied by quick jumps of H^+ protons from an H_3O^+ ion to an adjacent H_2O molecule, or from an H_2O molecule to OH^- ion.

$$OH_3^+ + OH_2 \rightarrow OH_2 + HOH_2^+ \text{ (in acid solutions)},$$

$$HO^- + HOH \rightarrow HOH + OH^- \text{ (in alcaline solutions)}$$

The aforementioned equations of equivalent conductance enable us to draw some interesting conclusions regarding the degree of dissociation of the electrolytes. On dividing the equation (III-19) by the equation (III-24) we obtain

$$\frac{\Lambda}{\Lambda^\circ} = \alpha \frac{v_+ + v_-}{v_+^\circ + v_-^\circ}. \qquad \text{(III-25)}$$

According to the Arrhenius theory the decrease of Λ with increasing concentration of the solution with all electrolytes is merely due to the lowering of the dissociation degree; as this theory does not take into account the mutual attraction of ions and the lowering of ion mobility in more concentrated solutions, the velocity of the ions in equation (III-25) should be equal both at finite concentrations and infinite dilution, i. e. $(v_+ + v_-) = (v_+^\circ + v_-^\circ)$. As a result of this the Arrhenius theory leads us to the conclusion:

$$\frac{\Lambda}{\Lambda^\circ} = \alpha, \qquad \text{(III-26)}$$

according to which it should be possible to calculate the degree of dissociation of an electrolyte from the ratio of Λ to Λ°. But it has already been demonstrated that the application of the Arrhenius theory to solutions of strong electrolytes has proved fundamentally incorrect, so that in such a case Λ/Λ° cannot be considered to represent the degree of dissociation. Rather it may be assumed a measure of the effect of interionic forces upon ionic velocities.

In case of the weak electrolytes the equation (III-26) can be applied only

to sufficiently diluted electrolytes when no account must be taken of the effect of electrostatic forces upon the velocity of ions. In the case of more concentrated solutions, however, the effect of such forces must be respected. To this end we start from the equation (III-19) and consider the term $F(v_+ + v_-)$ as the hypothetical equivalent conductance Λ' of a fully dissociated electrolyte ($\alpha = 1$) with an ion concentration equal to the ion concentration of a real solution of equivalent conductance Λ:

$$\alpha = \frac{\Lambda}{F(v_+ + v_-)} = \frac{\Lambda}{\Lambda'}. \qquad \text{(III-27)}$$

In this way we eliminate errors resulting from the application of equation (III-26), which is based on the assumption that ionic mobility is independent on the concentration of the solution. Equation (III-27) may be regarded as correct, because we compare now conductances of a partly dissociated (real) solution and of a fully dissociated (hypothetical) solution at the same ion concentration, in which case the interionic forces have the same influence upon the velocity of ions.

The method of calculating the degree of dissociation using equation (III-27) will be demonstrated for example by phosphoric acid of 0.1 gram-equivalent per litre concentration which dissociates to ions H^+ and $H_2PO_4^-$. Its equivalent conductance at infinite dilution and at 18 °C will be calculated according to the Kohlrausch law:

$$\Lambda^\circ = \Lambda^\circ_{(HCl)} + \Lambda^\circ_{(NaH_2PO_4)} - \Lambda^\circ_{(NaCl)} = 378.3 + 70.0 - 109.0 = 339.3 \text{ mho.}$$

A solution of acid of 0.1 gram-equivalent per litre concentration has a conductance $\Lambda = 96.5$ so that the degree of dissociation according to (III-26) α equals about $96.5/339.3 = 0.285$. According to this result the concentration of H^+ and $H_2PO_4^-$ ions in the solution considered is about 0.0285 gram-equivalents per litre. The hypothetical conductance of the solution with the same concentration of ions but with the electrolyte fully dissociated will be determined by another application of the Kohlrausch law using this time experimental data for the respective conductances of hydrochloric acid, sodium phosphate and sodium chloride (which are assumed to be fully dissociated); the data used are valid in all cases for the concentration of 0.0285 gram-equivalent per litre.

$$\Lambda' = 363.4 + 59.3 - 98.6 = 324.1 \text{ mho.}$$

Substituting this value into the equation (III-27) we obtain a more accurate value of the degree of dissociation $\alpha = 96.5/324.1 = 0.298$. A still more accurate value would be obtained on repeating the determination of Λ' using as a starting point the conductances of solutions of HCl, NaH_2PO_4 and NaCl with an equivalent concentration of 0.0298. The correction thus obtained is generally a very small one, so that no attention has to be paid to it in the case of less concentrated solutions.

Following the equation (III-25) the decrease of conductance of an electrolyte with increasing concentration is due to the lowering of the degree of dissociation on one hand and to lessening of the value of the fraction $(v_+ + v_-)/(v_+^\circ + v_-^\circ) = f_\Lambda$ on the other hand; this value f_Λ is called conductance coefficient and it expresses the effect of interionic forces upon the velocity of ions:

$$\frac{\Lambda}{\Lambda^\circ} = \alpha f_\Lambda. \tag{III-28}$$

Substituting the equation (III-27) into the equation (III-28) we obtain

$$f_\Lambda = \frac{\Lambda'}{\Lambda^\circ}. \tag{III-29}$$

The value of the fraction representing the ratio of the conductances of two differently concentrated but fully dissociated solutions can be calculated from Onsager's equation (see III-14) which enables us to determine the effect of electrostatic forces of attraction in strong, i. e. fully dissociated electrolytes. In the case of weak electrolytes, however, it is necessary to substitute c_e in Onsager's equation by the real concentration of ions, i. e. by αc_e and to replace the symbol Λ by Λ', which means that the equivalent conductance of a hypothetical, fully dissociated solution is considered. In this way we obtain the following equation:

$$f_\Lambda = \frac{\Lambda'}{\Lambda^\circ} = 1 - \frac{k}{\Lambda^\circ}\sqrt{\alpha c_e}. \tag{III-30}$$

After the substitution of this relation into the equation (III-28) a corrected Arrhenius equation results:

$$\frac{\Lambda}{\Lambda^\circ} = \alpha\left[1 - \frac{k}{\Lambda^\circ}\sqrt{\alpha c_e}\right]. \tag{III-31}$$

In the case of strong electrolytes with $\alpha = 1$ the last mentioned equation changes to the form of Onsager's equation, while for very weak electrolytes or substantially diluted solutions ($c_e \cong 0$, $f_\Lambda \cong 1$) it changes to the classical formula of Arrhenius. If we consider the problem of electrolytes from the point of view of the equation (III-31) we can see that there is no sharp dividing line between strong and weak electrolytes. It can equally be seen that the Debye-Hückel-Onsager theory does not replace the theory of Arrhenius but merely corrects and suitably supplements it.

IV. TRANSFERENCE NUMBERS

It has been already said that the conduction of electricity in an electrolyte is due to both anions and cations. The part of the total quantity of electricity transferred by each of the two species respectively depends on the relative velocity of the anions and the cations. Evidence to this can be gained from the following calculations.

If the equation (III-19) is substituted in the equation (III-10) then the total current flowing through the electrolyte can be determined by using the following equation:

$$I = \frac{Ec_e\, q\Lambda}{1000\, l} = \frac{Ec_e\, qF\, \alpha\, (v_+ + v_-)}{1000\, l}. \qquad \text{(IV-1)}$$

From the total current part I_+ is transferred by the cation and part I_- by the anion (see also III-21):

$$I_+ = \frac{Ec_e\, q\lambda_+}{1000\, l} = \frac{Ec_e\, qF\, \alpha v_+}{1000\, l} \qquad \text{(IV-2)}$$

$$I_- = \frac{Ec_e\, q\lambda_-}{1000\, l} = \frac{Ec_e\, qF\, \alpha v_-}{1000\, l}. \qquad \text{(IV-3)}$$

Designating the part of the total current transferred by cation as t_+ and the part transferred by anion as t_- then dividing the equations (IV-2) an (IV-3) by (IV-1) we get the following important formulae:

$$t_+ = \frac{I_+}{I} = \frac{\lambda_+}{\Lambda} = \frac{v_+}{v_+ + v_-} \qquad \text{(IV-4)}$$

$$t_- = \frac{I_-}{I} = \frac{\lambda_-}{\Lambda} = \frac{v_-}{v^+ + v_-}. \qquad \text{(IV-5)}$$

The values t_+ and t_- are called transference numbers of cation and anion; the tables contain only the values of t_+ as the value of $t_- = 1 - t_+$. By dividing the last two equations we find that the ratio of the transference numbers equals the ratio of mobilities of both ions or the ratio of their ionic conductances. Only if the velocity of both ions is identical will equal quantities of electricity be transferred by both anions and cations.

The equations (IV-4) and (IV-5) enable us to determine the equivalent conductances of individual ions from measured transference numbers and from the equivalent conductance of the solution.

$$\lambda_+ = t_+\Lambda \qquad \text{(IV-6a)}$$

$$\lambda_- = t_-\Lambda. \qquad \text{(IV-6b)}$$

Analogous equations can be applied to the equivalent conductances of individual ions in infinitely diluted solutions:

$$\lambda_+^\circ = t_+^\circ \Lambda^\circ \qquad \text{(IV-7a)}$$

$$\lambda_-^\circ = t_-^\circ \Lambda^\circ \qquad \text{(IV-7b)}$$

where t_+° and t_-° stand for the transference numbers at infinite dilution which can be determined by extrapolation. If from the last two equations the values of λ_+° and λ_-° are ascertained the absolute velocities of ions in infinitely diluted solutions can be calculated using the corresponding equations (III-24).

Unequal velocities of ions cause changes in concentrations in the proximity of electrodes. From these changes the transference numbers can be calculated provided the quantity of electricity passed through the electrolyte is known (Hittorf's method).

The measurement is effected in a simple glass apparatus usually consisting of three U-shaped tubes connected one after onother and filled with the solution to be examined. Platinum electrodes are fitted into two external tubes. After a definite quantity of electricity, which is to be ascertained by means of a coulometer connected into the circuit, has been allowed to pass through the apparatus, the individual tubes are separated and the change of composition in each of them determined. The unchanged concentration of the solution in the middle U-tube is proof of the correctness of the measurement. The transference numbers are then calculated from the ascertained changes of composition within the outer tubes by using the following formulae:

$$\frac{\text{decrease in the number of equivalents of the cation at the anode due to migration}}{\text{number of equivalents proportionate to current passed}} = t_+$$

$$\frac{\text{decrease in the number of equivalents of the anion at the cathode due to migration}}{\text{number of equivalents proportionate to current passed}} = t_-.$$

Electrochemical processes at the electrodes also cause changes in the composition of the anolyte. Such changes can be calculated by the application of Faraday's law. In order to determine the decrease in numbers of equivalents of cation and anion due solely to migration, total change in concentration must be quantitatively corrected in view of the above effects of electrochemical processes.

Another way of determining the transference numbers is moving boundary methode, whereby the movement of a visible boundary between two solutions of different electrolytes in an electrical field is followed by observing the colour or light refraction. If for instance a solution of potassium permanganate is in contact with a solution of potassium nitrate the displacement of colored

MnO_4^- ions on the passage of the current can be clearly seen. Finally the transference numbers, thus also the mobility of ions can be determined by the measurement of electromotive forces of suitably combined cells.

The transference numbers of some electrolytes are given in Table 7. It can be seen that their value varies widely.

Table 7. Transference numbers of cations (at 25 °C)

Electrolyte	0,01N	0,05N	0,1N	Electrolyte	0,01N	0,05N	0,1N
HCl	0,825	0,829	0,831	$K_3Fe(CN)_3$	0,431	0,439	0,441
H_2SO_4	—	0,822	0,822	$CaCl_2$	0,426	0,414	0,406
KNO_3	0,508	0,509	0,510	NaCl	0,392	0,388	0,385
NH_4Cl	0,491	0,491	0,491	$CdSO_4$	0,389	0,374	0,364
KCl	0,490	0,490	0,490	$CuSO_4$	—	0,375	0,373
KBr	0,483	0,483	0,483	LiCl	0,329	0,321	0,317
$AgNO_3$	0,465	0,466	0,468	NaOH	0,203	0,189	0,183

The extreme values of acids and bases indicate some extra high mobility of ions H^+ and OH^-. The effect of temperature manifests itself in such a way that with increasing temperature the transference numbers approach a limit value of 0.5; this means that the transference numbers above 0.5 decrease and the ones below that value increase. The transference numbers do not depend on the current passing through the electrolyte, yet change somewhat with the concentration. The values which are high in a diluted solution usually increase with increasing concentration while the lower ones decrease.

Hittorf's transference numbers determined from the change in concentration of the electrolyte near the electrodes include a certain error, because due to the hydration of the ions the migration is accompanied by the transport of water which changes the composition of the solution near the electrodes.

On determining experimentally the number of moles of water transported and correcting Hittorf's transference numbers t_+ accordingly, we obtain the true transference numbers $(t_+)_{true}$. Both values valid for cations of some electrolytes at 25 °C and in 1.3 N - solution are indicated in the following table:

	HCl	KCl	NaCl	LiCl
$(t_+)_{true}$	0,844	0,495	0,383	0,304
t_+	0,82	0,482	0,366	0,278

V. LAWS OF CHEMICAL EQUILIBRIUM

One of the main problems of electrochemistry is the study of conditions concerning the conversion of chemical energy into electrical and vice versa. Quantitative relations between both forms of energy are based on exact thermodynamical laws which can be applied, if the process occurs reversibly. These laws, therefore, enable to determine the amount of energy to be gained or spent in a reversible course of a reaction, if the thermodynamical properties of the reacting system are known.

A. FUNDAMENTALS OF THERMODYNAMICS

If a chemical process under consideration, expressed by a common equation

$$aA + bB + \ldots = lL + mM + \ldots, \qquad \text{(V-1)}$$

is to proceed spontaneously in the direction from left to right, it is necessary that the energetic level of the system prior to reaction is higher than the energetic level of the reaction products. In other words a reaction takes place if accompanied by a liberation of energy capable to perform useful work, e. g. electrical work. The quantity of energy which can be gained in the course of a reaction depends on the conditions under which the process is allowed to proceed. A maximum of work is gained in a system, in which the force causing chemical changes is almost entirely counterbalanced by another external force acting against the course of the reaction and in which all energy losses are eliminated. By a slight increase of the counterbalancing external force the course of the reaction can be reversed and the system brought to its initial state. Such processes are therefore called reversible processes. If the reaction takes place at constant temperature and pressure, the value of the maximum work equals the change of the thermodynamic quantity called free energy of the reacting system expressed in calories. The change in free energy ΔG, which takes place during a chemical reaction, can be expressed as a difference between the free energy of the system after the reaction G_2 and before the reaction G_1. From the knowledge of change ΔG we can conclude whether the process in question can take place spontaneously or not. The free energy of a system prior to reaction can be calculated as the sum of products of the so called chemical potentials of individual substances μ and of the number of their moles or gram-atoms (or gram-ions) entering into the reaction:

$$G_1 = a\mu_A + b\mu_B + \ldots \qquad \text{(V-2)}$$

Similarly the free energy of a system after reaction can be expressed as:

$$G_2 = l\mu_L + m\mu_M + \ldots \qquad \text{(V-3)}$$

On substracting G_2 from G_1 we obtain the change in free energy of the system:

$$(\Delta G)_{P,T} = G_2 - G_1 = l\mu_L + m\mu_M + \ldots - a\mu_A - b\mu_B. \qquad \text{(V-4)}$$

It has been already said that the condition of the spontaneity of a reaction is the possible transfer of a certain quantity of energy to the surroundings, the maximum of which being equivalent at constant pressure and temperature to the decrease in the free energy of the system. A characteristic feature of all thermodynamically feasible and spontaneously occurring processes is therefore expressed as follows:

$$(\Delta G)_{T,P} < 0. \qquad \text{(V-5)}$$

In electrochemistry all galvanic cells and storage batteries belong to systems satisfying this condition.

If on the other hand the value of ΔG is positive or:

$$(\Delta G)_{T,P} > 0, \qquad \text{(V-6)}$$

the reaction cannot proceed from left to right spontaneously. Such a reaction can be, however, forced to proceed in the desired direction if we succeed in performing it within an electrolyzer and supply the energy lacking from an external source in the form of electrical current.

If finally both, reaction products and reactants, are present in the system at equal energetic levels (there is no difference between the free energies of products and reactants) no reaction can occur in any direction. In such a case we speak of an equilibrium between the reactants and the reaction products, which can be expressed (at condition of constant temperature and pressure) by the following equation:

$$(\Delta G)_{T,P} = 0 \qquad \text{(V-7)}$$

These three possible values of changes in free energy which can be considered a measure of the driving force, i. e. the affinity of chemical processes, are an important criterion of the state of equilibrium and of the direction in which the desired reaction can proceed spontaneously under given working conditions and a sufficient reaction velocity.

It will be seen from equations (V-2) and (V-3) that in order to calculate the changes in free energy we have to know the chemical potentials of individual reaction components. Regarding the question of pure compounds forming separate phases, the potential is understood to be the molal free energy related to one mole (gram-ion or gram-atom) of the substance and depends solely upon the chemical nature of the substance, its physical state and upon temperature and pressure. In the case of solutions of gaseous, liquid or solid substances, however, the conception of the potential of the solute is more complicated because its value apart from depending on the above mentioned factors is also a function of the composition of the solution. From the thermodynamical point of view the chemical potential of a dissolved substance thus

represents the change in the total free energy of an infinite amount of a solution at a given concentration which takes place, if one mole of the substance under consideration is added to it, while pressure, temperature and number of moles of all other components are kept constant. The potential so defined of the dissolved substance, sometimes called partial molal free energy, depends on the instantaneous composition of the solution, other conditions being constant.

Unlike free energy G, which is an extensive property (such as for example volume or internal energy), chemical potential μ is an intensive property of the system (such as e. g. temperature and pressure). For this reason the chemical potential of the solute at given temperature and pressure does not depend on the absolute amounts of individual components in the solution but solely on the relative composition, i. e. relative amounts of the substances forming the solution.

As absolute values of free energies and potentials of substances are not known, we can only quote the differences between the values belonging to them in concrete cases and the values related to a certain, so called standard state. Values of other thermodynamic functions, such as internal energy, enthalpy, etc. are quoted in the same way. As the standard state of pure liquid or solid substances we consider their state in stable modification at 1 atm. pressure and at the temperature of the system. As the standard state for gas, either alone or in a mixture, the state of a pure gas in ideal state is taken at 1 atm. pressure and at the temperature of the system.

When choosing the standard state for liquid or solid solutions we distinguish between the solute and the solvent. For the component which predominates in the solution i. e. for the solvent, the state of pure liquid compound at the temperature of the system and the pressure of 1 atm. is almost generally chosen.

On the other hand the standard state of a dissolved substance, which behaves in the solvent as a nonelectrolyte, is defined as its state in a hypothetical ideal solution containing one mole of the substance in 1000 grams of solvent (i. e. with a concentration in terms of molality, $m = 1$). In this solution some properties of the dissolved substance are the same as in an infinitely diluted solution In other cases the hypothetical standard state of the dissolved substance is used in which 1 mole of the substance is contained in one liter of the ideal solution (i. e. the concentration is expressed in terms of molarity, $c = 1$).

For solutions of electrolytes the standard state is derived from an analogous hypothetical state of the ideal solution; it will be shown later that when indicating the concentration of such a solution even the valences of ions formed on the dissociation should be considered.*)

When calculating the total change in the free energy accompanying a certain chemical reaction the so called standard free energies of formation of

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*) Apart from previously mentioned states, other standard states also are used. In this book only the most common states in electrochemistry are mentioned.

compounds are used which have been derived under the assumption that molal free energies of all elements in their standard state equal zero at all temperatures. In this sense the standard molal free energy of the formation of a compound is identical with the standard free energy of its formation from elements being also in their standard states. Standard molal free energies of formation of ions are also known which express the difference between their standard chemical potentials and the standard potentials of the elements composing them. The calculation of free energy of formation of ions is based on the convention that the standard free energy of hydrogen ions equals zero. As free energy is an additive property of the system (see equation V-4), the change in the standard free energy of a certain reaction can be calculated by adding and substracting standard free energies of formation of individual compounds as in calculations of heats of reaction. The values of standard molal free energies of formation of many substances at 25 °C are contained in tables. It is obvious that this rule concerning the additive character of free energy can be applied for the calculations of the total change in free energy of a reaction also in cases, where the substances taking part in the reaction are not in their standard states.

The relation between the potential of a substance in any arbitrary state and the potential of the same substance in the standard state can be expressed by a particular quantity called activity. According to the definition of this quantity any substance in its standard state possesses an activity equal to unity. If then the activity of the same substance in a state other than standard is characterized by an activity equal to a, the relation between the potential in the later state μ and the potential in the standard state μ_0 can be expressed by following equation

$$\mu = \mu^\circ + RT \ln a.^*) \tag{V-8}$$

The activity is expressed mathematically by the ratio of thermodynamically effective pressures of a given substance in any arbitrary state (the so called fugacity f) and of the corresponding value in the standard state (fugacity f°), at constant temperature:

$$a = \left(\frac{f}{f^\circ}\right)_T. \tag{V-8a}$$

As fugacity can be considered, from the point of view of its physicochemical meaning, a tendency of the substance to escape from the given system and to pass over into another system, it actually expresses how many times this property of a substance in a given state is strengthened or weakened in comparison with the standard state. At a suitable choice of the standard states in individual cases and under the assumption of the ideal behavior of the sub-

*) In this equation R stands for the universal gas constant, the numerical value of which is:

$$R = 1.987 \text{ cal/°K mole}$$

stance the conception of activity of gases (both single, or in mixtures) has the same meaning as their partial pressures; the activity of substances in liquid solutions coincides then with their analytically expressed concentrations (see further). The same is valid approximately also for the real gaseous mixtures and liquid solutions provided they have been sufficiently diluted. The higher the partial pressures of gases or the more concentrated the solutions, the greater the difference between the above mentioned quantities. In order to facilitate the use of pressures or concentrations as easily measurable quantities in chemical equations the term activity coefficient γ has been introduced; these coefficients represent correction factors by which the above mentioned quantities have to be multiplied to obtain the activities determining the thermodynamic behavior of a substance in a given system. The numerical value of an activity coefficient depends, apart from the nature of the solution, its temperature and pressure, also on the composition of the gaseous mixture or solution; it can be easily conceived that the magnitude of its deviation from unity indicates to what degree the behaviour of gaseous mixtures or liquid solutions differs from that of the ideal mixtures or solutions.

The conception of activity has a special importance in electrochemistry as in case of solutions of electrolytes the behavior of ions changes already at rather low concentrations due to the effect of electrostatic forces; as a result of this, the value of the corresponding activity coefficients drops below unity.

At higher concentrations the activity of ions can be influenced by their association and by a change in the nature of the solvent as well as by the interaction of ions and molecules of the solvent. All these factors might cause a rise in the activity coefficient after an initial drop to a certain minimum; at higher concentrations the value of the coefficient even exceeds unity.

Activity coefficients will be discussed in more detail when dealing with individual types of reaction. Meanwhile we shall derive an important equation concerning common chemical equilibrium by the application of the activities of reaction components.

The equation (V-4) expresses the difference in free energy of a system after reaction and before it on the assumption that the individual components are in arbitrary states. By a similar equation we can express the change in the standard free energy of the same reaction when both reactants and reaction products are in the standard state:

$$(\Delta G^\circ)_T = l\mu_L^\circ + m\mu_N^\circ + \ldots - a\mu_A^\circ - b\mu_B^\circ - \ldots^*) \qquad \text{(V-9)}$$

From the difference between equations (V-4) and (V-9) we obtain the following equation

*) If the state of reaction components at a fixed constant pressure (generally at 1 atm) is considered as their standard state, the value of ΔG° depends only on the temperature. Therefore the symbol of the change in standard free energy ΔG°_T is marked by the suffix T contrary to the symbol of the change in free energy $\Delta G_{T,P}$, which depends on both, temperature and pressure.

$$(\Delta G)_{T,P} - (\Delta G^\circ)_T = l(\mu_L - \mu_L^\circ) + m(\mu_M - \mu_M^\circ) + \ldots - \\ - a(\mu_A - \mu_A^\circ) - b(\mu_B - \mu_B^\circ) - \ldots \quad \text{(V-10)}$$

If by means of equation (V-8) the difference of potentials of individual components is expressed by corresponding values of activities, we obtain

$$(\Delta G)_{T,P} - (\Delta G^\circ)_T = RT\ln \frac{(a_L)^l (a_M)^m \ldots}{(a_A)^a (a_B)^b \ldots}. \quad \text{(V-11)}$$

In this equation a_A and a_B etc. stand for respective activities of substances entering the reaction or resulting from it.

Finally on substituting the equilibrium condition $(\Delta G)_{P,T} = 0$ (see V-7) into the equation (V-11) the values of activities can be considered to be the activities of the reaction components in the equilibrium state $[(a_A)_r, (a_B)_r$ etc.]. The equation obtained then applies to the state when all substances have lost their capability to react further and their concentration has attained the equilibrium state

$$(\Delta G^\circ)_T = -RT\ln \frac{(a_L)_r^l (a_M)_r^m \ldots}{(a_A)_r^a (a_B)_r^b \ldots}, \quad \text{(V-12)}$$

$(\Delta G^\circ)_T$ being constant at a given temperature the equation (V-12) can also be written in the following form:

$$(\Delta G^\circ)_T = -RT \ln K \quad \text{(V-13)}$$

where K denotes the thermodynamical equilibrium constant of the reaction which is a function of temperature but not of pressure, provided the standard state of the substances has been defined accordingly (i. e. at a definite constant pressure e. g. 1 atm.):

$$K = \frac{(a_L)_r^l (a_M)_r^m \ldots}{(a_A)_r^a (a_B)_r^b \ldots}. \quad \text{(V-14)}$$

The last equation, one of the most important physicochemical equations, expresses exactly the law of mass action, formulated for the first time by *Guldberg* and *Waage* in a less exact form. The equation enables the calculation of the equilibrium composition of a reaction mixture or determination of theoretically possible yields of chemical processes starting from the known value of the equilibrium constant K which can be determined by thermodynamic methods.

To enable the application of the law of mass action to actual problems the activities appearing in equation (V-14) have to be substituted by directly measurable quantities (such as pressures or concentrations). To achieve this we use different suitable standard states according to the character of the process in order to obtain a simple relation between activity and pressure (or concentration). In the following chapter the selection of the most suitable standard states in individual cases will be discussed.

B. GASEOUS SYSTEMS

It has already been mentioned that the state of an ideal gas at the temperature of the system and the pressure of 1 atmosphere is most frequently chosen as the standard state of gases. The idea of such an ideal gas can be explained by the imagination of a real gas which is first expanded to zero pressure and then by means of isothermal compression compressed to 1 atm. into the region of the ideal gas. As with an ideal gas pressure equals fugacity, we can substitute in equation (V-8a) $p^\circ = f^\circ = 1$, whereby the following equation is obtained:

$$a_p = \frac{f}{f^\circ} = f. \tag{V-15}$$

From this it can be concluded, that for a selected standard state the activity of a gas equals its fugacity.

The fugacity, considered as the thermodynamically effective pressure f, equals the measured pressure p exactly in the case of ideal gases only. In the case of real gases both values differ by the so called activity coefficient γ_p, the value of which depends on the given state of the gas:

$$a_p = f = p\gamma_p. \tag{V-16}$$

The lower the pressure of real gases the nearer their behavior to that of ideal gases; the following equation can be written for the limit of infinitely low pressure:

$$(\gamma_p)_{p\to 0} = \left(\frac{a_p}{p}\right)_{p\to 0} = \left(\frac{f}{p}\right)_{p\to 0} = 1 \tag{V-17}$$

$$a_p = f = p \text{ (for } p \to 0). \tag{V-18}$$

According to the last equation the activities of gases at infinitely low pressures can be substituted in the equation of the law of mass action by corresponding partial pressures. It has been shown that such a substitution is permissible even at middle low pressures (i. e. about 1 atm.) provided the temperature of the gas is sufficiently above its temperature of liquefaction. Unless this condition is satisfied the activity of gases must be substituted in principle by the product of their partial pressures and corresponding activity coefficients according to equation (V-16).

C. HETEROGENOUS SYSTEMS

When pure solids or liquids, which do not form any solution, participate in a reaction beside gases, the standard state for gases is chosen the same as described in the preceding chapter, while the standard state of the condensed components is defined by their state at 1 atm pressure and at the temperature of the system. Activity of liquid and solid substances varies only very slightly with pressure

as compared with the activity (fugacity) of gases so that their values equal practically unity even at pressures different from 1 atm. Therefore, in the equation of the corresponding equilibrium constant appear only the activities of the gaseous components, but not the activities of solids and liquids. If the solids and liquids would be present as components of solid or liquid solutions, their activity would not equal unity any longer, and their participation in the reaction ought to be considered also in the equation of the law of mass action. In such a case it would be necessary to choose as the standard state of the dissolved substances some of the states applicable to solutions mentioned later.

It is evident from this explanation that where substances react in different states a standard state that best accords with their nature has to be chosen for each of them.

D. SOLUTIONS OF NONELECTROLYTES

For the predominant component of a solution, i. e. the solvent, the state of the pure liquid at the temperature of the system and the pressure of 1 atm. is chosen as the standard state. In so far as sufficiently diluted solutions are concerned (i. e. such solutions the composition of which differs but slightly from the pure solvent) the solvent can be considered to follow approximately Raoult's law valid for ideal solutions, according to which the fugacity f of the solvent in a solution can be expressed as the product of its molar fraction N_1*) and of the fugacity of the pure liquid substance f_1' at the same temperature, thus:

$$f_1 \cong N_1 f_1'.** \tag{V-19}$$

On substituting this relation into equation (V-8a) we obtain:

$$a_N = \frac{f_1}{f_1^\circ} \cong \frac{N_1 f_1^\circ}{f_1^\circ} \cong N_1, \tag{V-20}$$

according to which the activity of a solvent in diluted solutions can be simply substituted in the equation of the equilibrium constant by the corresponding mole fraction.

For more concentrated solutions Raoult'slaw is no longer applicable and the molar fraction N_1 of the solvent must be multiplied by the activity coefficient γ_N, thus respecting the deviations from the ideal behavior of solutions:

$$a_N = N_1 \gamma_N \tag{V-21}$$

*) The molar fraction of a substance in a solution is expressed by the ratio of moles of that substance to the sum of moles of all substances present in the solution, for example:

$$N_1 = \frac{n_1}{n_1 + n_2 + \ldots}.$$

**) Index 1 marks the solvent, index 2 the solute.

It will be readily understood that the higher the value of N_1, i. e. the more diluted the solution, the smaller the difference of the activity coefficient from unity, so that in the limit case of an infinitely diluted solution we arrive at the equation:

$$(\gamma_N)_{N1 \to 1} = \left(\frac{a_N}{N_1} \right)_{N1 \to 1} = 1 , \tag{V-22}$$

which corresponds to the equation (V-20) if used for very diluted solutions.

As the molar fraction of the solvent (e. g. of water) in such solutions differs very slightly from unity, the activity of the solvent must also practically equal unity and, therefore, it does not appear in the equation which expresses the law of mass action.

For dissolved substances (nonelectrolytes), present in solutions in lesser quantities, the state of a hypothetical ideal solution with a molality $m = 1$ or a molarity $c = 1$ is usually chosen as the standard state. These standard states are derived by extrapolation from the reference state of an infinitely diluted real solution, in which the activity of the solute equals the molality or molarity, to the region of the ideal solution of unit concentration.

In case of sufficiently diluted solutions the solute approximately follows the law of *Henry* according to which its fugacity f_2 is directly proportional to its molal (m_2) or molar (c_2) concentration, thus

$$f_2 \cong k_2 m_2 \tag{V-23a}$$

or

$$f_2 \cong k_2' c_2. \tag{V-23b}$$

As for the standard state $m_2 = 1$ ($c_2 = 1$), we can write:

$$f_2^\circ = k_2 \tag{V-24a}$$

or

$$f_2^\circ = k_2'. \tag{V-24b}$$

Substituting the last mentioned relation into the equation (V-8a), we obtain the equations:

$$a_m = \frac{f_2}{f_2^\circ} \cong \frac{k_2 m_2}{k_2} \cong m_2 \tag{V-25a}$$

or

$$a_c = \frac{f_2}{f_2^\circ} \cong \frac{k_2' c_2}{k_2'} \cong c_2, \tag{V-25b}$$

according to which it is possible, in the case of sufficiently diluted solutions, to substitute the activities of substances dissolved into the equation of the equilibrium constant (see the equation V-14), by corresponding concentrations expressed in terms of molality or molarity.

In case of more concentrated solutions it is, however, necessary to multiply the analytical concentration by the corresponding activity coefficient, as its value differs considerably from unity:

$$a_m = m_2\gamma_m \tag{V-26a}$$

or

$$a_c = c_2\gamma_c. \tag{V-26b}$$

In extreme cases of infinitely diluted solutions, where $m_2 \to 0$ (or $c_2 \to 0$) and $\gamma_m = 1$ (or $\gamma_c = 1$), the last mentioned equations transform themselves to equations (V-25a, b).

E. SOLUTIONS OF ELECTROLYTES

1. Strong electrolytes

Strong electrolytes are considered to be completely dissociated in their solutions and their deviations from ideal behavior are ascribed to the effect of the strong forces of attraction acting between the oppositely charged ions. As in such solutions there are no undissociated molecules apart from ions, no equilibrium is established to which the law of mass action could be applied. The potential μ_2 of the electrolyte as a whole dissociated according to the formula

$$A_{\nu_+}B_{\nu_-} = \nu_+A^{z+} + \nu_-B^{z-} \tag{V-27}$$

is, therefore, described for purely formal reasons by the sum of products of the number of gram-ions ($\nu_+\nu_-$) produced on dissociation of one mole of the electrolyte and of their potentials (μ^+, μ^-):

$$\mu_2 = \nu_+\mu_+ + \nu_-\mu_-. \tag{V-28}$$

The electrolyte in the standard state is also supposed to be fully dissociated, so that even in this case the potential μ_2° of the electrolyte as a whole can be expressed as the sum of products of the number of gram-ions, formed on dissociation of one mole of the electrolyte and of their standard potentials:

$$\mu_2^\circ = \nu_+\mu_+^\circ + \nu_-\mu_-^\circ. \tag{V-29}$$

On substituting into the equations (V-28) and (V-29) the relations between different potentials in accordance with (V-8)

$$\mu_2 = \mu_2^\circ + RT\ln a_2 \tag{V-30}$$

$$\mu_+ = \mu_+^\circ + RT\ln a_+ \tag{V-31}$$

$$\mu_- = \mu_-^\circ + RT\ln a_-, \tag{V-32}$$

we arrive at a basic equation which defines the activity a_2 of a strong electrolyte as a whole by means of the activity of the ions of which it is composed:

$$a_2 = a_+^{\nu_+}\, a_-^{\nu_-} \tag{V-33}$$

As the activity of individual ions cannot be determined separately, the con-

ception of the mean activity $a \pm m$ has been introduced, expressed by a geometrical mean value of the individual activities:

$$a_{\pm m} = \left[a_+^{\nu_+} a_-^{\nu_-} \right]^{\frac{1}{\nu}} \tag{V-34}$$

where $\nu = \nu_+ + \nu_-$.

If the concentration of an electrolyte in its standard state is expressed by its molality, the following equations can be written for the activity coefficients in a concrete solution

$$\gamma_+ = \frac{a_+}{m_+} \text{ and } \gamma_- = \frac{a_-}{m_-}. \tag{V-35}$$

As the values of the activity coefficients of individual ions are not known, the so called mean activity coefficient $\gamma_{\pm m}$ is used which is defined as follows:

$$\gamma_{\pm} = \left[\gamma_+^{\nu_+} \gamma_-^{\nu_-} \right]^{\frac{1}{\nu}}. \tag{V-36}$$

For reasons of symmetry another function has been introduced for electrolytes, namely the so called mean ionic molality $m_{\pm}$ defined by the equation:

$$m_{\pm} = \left[m_+^{\nu_+} m_-^{\nu_-} \right]^{\frac{1}{\nu}} = m \left[\nu_+^{\nu_+} \nu_-^{\nu_-} \right]^{\frac{1}{\nu}} \tag{V-37}$$

where m stands for the analytical molality, so that

$$m_+ = \nu_+ m \text{ and } m_- = \nu_- m.$$

When defining the standard state of an electrolyte in solution we start from the reference state of each individual ion in an infinitely diluted solution, in which the activity of the ions is assumed to be equal to the corresponding molality, or their activity coefficient is assumed to equal unity:

$$(\gamma)m_{+\to 0} = \left(\frac{a_+}{m_+} \right) m_{+\to 0} = 1$$

$$(\gamma)m_{-\to 0} = \left(\frac{a_-}{m_-} \right) m_{-\to 0} = 1.$$

The reference state can be expressed with due regard to the equations (V-34), (V-36) and (V-37) also by a common equation

$$(\gamma_{\pm m})m_{\pm\to 0} = \left(\frac{a_{\pm m}}{m_{\pm}} \right) m_{\pm\to 0} = 1, \text{ or } a_{\pm m} = m_{\pm} \text{ (for } m_{\pm} \to 0). \tag{V-38}$$

The properties of the state thus defined are then extrapolated in a linear

way to the region of the standard state of ideal solution in which the concentration of the electrolyte satisfies the condition:

$$m_{\pm} = a_{\pm m} = 1 \text{ (when } \gamma_{\pm m} = 1).$$

It can be concluded from equation (V-37) that the analytical concentration corresponding to such a standard solution can be expressed as:

$$m = \left[\nu_+^{\nu+}\, \nu_-^{\nu-}\right]^{-\frac{1}{\nu}}$$

On substituting the equations (V-34) to (V-37) into the equation (V-33) we obtain an important expression determining the relation between the activity of an electrolyte and its concentration in a given solution:

$$a_2^{\frac{1}{\nu}} = a_{\pm m} = m_{\pm}\, \gamma_{\pm m} = m\, [\nu_+^{\nu+}\, \nu_-^{\nu-}]\, \gamma_{\pm m} \qquad \text{(V-39)}$$

The dependence between a_2 and $a_{\pm m}$ on the one hand and concentrations m as well as activity coefficient $\gamma_{\pm}$ on the other hand for different electrolytes can be seen from the following table:

Type of electrolyte	Substance	ν_+	ν_-	ν	$m_{\pm}$	$a_{\pm m} = m_{\pm}\gamma_{\pm m}$	$a_2 = a^{\nu}{}_{\pm m}$
1–1	HCl	1	1	2	m	$m\gamma_{\pm}$	$m^2\gamma_{\pm}^2$
2–2	$MgSO_4$	1	1	2	m	$m\gamma_{\pm}$	$m^2\gamma_{\pm}^2$
3–3	$AlPO_4$	1	1	2	m	$m\gamma_{\pm}$	$m^2\gamma_{\pm}^2$
1–2	H_2SO_4	2	1	3	$\sqrt[3]{4}\, m$	$\sqrt[3]{4}\, m\gamma_{\pm}$	$4\, m^3\gamma_{\pm}^3$
2–1	$BaCl_2$	1	2	3	$\sqrt[3]{4}\, m$	$\sqrt[3]{4}\, m\gamma_{\pm}$	$4\, m^3\gamma_{\pm}^3$
1–3	Na_3PO_4	3	1	4	$\sqrt[4]{27}\, m$	$\sqrt[4]{27}\, m\gamma_{\pm}$	$27\, m^4\gamma_{\pm}^4$
3–1	$La(NO_3)_3$	1	3	4	$\sqrt[4]{27}\, m$	$\sqrt[4]{27}\, m\gamma_{\pm}$	$27\, m^4\gamma_{\pm}^4$
2–3	$Ca_3(PO_4)_2$	3	2	5	$\sqrt[5]{108}\, m$	$\sqrt[5]{108}\, m\gamma_{\pm}$	$108\, m^5\gamma_{\pm}^5$
3–2	$La_2(SO_4)_3$	2	3	5	$\sqrt[5]{108}\, m$	$\sqrt[5]{108}\, m\gamma_{\pm}$	$108\, m^5\gamma_{\pm}^5$

Analogously, an electrolyte in the state of an ideal solution of a mean molarity $c_{\pm} = 1$ can be chosen as the standard state, and the following equation can be arrived at:

$$a_{\pm c} = c_{\pm}\gamma_{\pm c}, \qquad \text{(V-40)}$$

as well as other equations similar to the aforementioned one with the exception that for $m_{\pm}$, $a_{\pm m}$ and $\gamma_{\pm m}$ it is necessary to substitute $c_{\pm}$, $a_{\pm c}$ and $\gamma_{\pm c}$. In sufficiently diluted solutions the following relationships are valid between the individual quantities:

$$c_{\pm} \cong m_{\pm}\rho^{\circ} \tag{V-41a}$$

$$a_{\pm c} \cong a_{\pm m}\rho^{\circ} \tag{V-41b}$$

$$\gamma_{\pm c} \cong \gamma_{\pm m} \tag{V-41c}$$

where ρ° stands for the density of the solvent (e. g. water).

The activity a_2 of an electrolyte can be derived from the difference in behavior of real solutions and ideal solutions. For this purpose measurements are made of electromotive forces of cells, depression of freezing points, elevation of boiling points, solubility of electrolytes in mixed solutions and other characteristic properties of solutions. From the value of a_2 thus determined the mean activity $a_{\pm}$ is calculated using the equation (V-38) whereupon by application of the analytical concentration the activity coefficient $\gamma_{\pm}$ is finally determined. The activity coefficients for sufficiently diluted solutions can also be calculated directly on the basis of the Debye-Hückel theory, which will be explained later on.

Table 8. Mean activity coefficients of electrolytes in aqueous solutions at 25 °C

Concentration in moles per 1000 g . H_2O	NaCl	KCl	HCl	NaOH	$CaCl_2$	$ZnCl_2$	H_2SO_4	$ZnSO_4$	$CdSO_4$
0,005	0,928	0,927	0,930	–	0,789	0,767	0,643	0,477	0,476
0,01	0,903	0,902	0,906	0,899	0,732	0,708	0,545	0,387	0,383
0,02	0,872	0,869	0,878	0,860	0,669	0,642	0,455	0,298	–
0,05	0,821	0,817	0,833	0,805	0,584	0,556	0,341	0,202	0,199
0,10	0,778	0,770	0,798	0,759	0,524	0,502	0,266	0,148	0,137
0,20	0,732	0,719	0,768	0,719	0,491	0,448	0,210	0,104	0,104
0,50	0,680	0,652	0,769	0,681	0,510	0,376	0,155	0,063	0,061
1,00	0,656	0,607	0,811	0,667	0,725	0,325	0,131	0,044	0,042
1,50	0,655	0,587	0,898	0,671	–	0,290	–	0,037	0,039
2,00	0,670	0,578	1,011	0,685	1,554	–	0,125	0,035	0,030
3,00	0,719	0,574	1,31	0,784	3,384	–	0,142	0,041	0,026
4,00	0,791	–	1,74	0,903	–	–	0,172	–	–
5,00	0,874		2,38	1,077			0,212		
6,00	0,986		3,22	1,299			0,264		

The mean activity of some of the most important strong electrolytes at various molal concentration in aqueous solutions at 25° C are given in Table 8. In Fig. 6 the values of mean activity coefficients $\gamma_{\pm}$ are shown as a function of the square root of molality $\sqrt{m}$.

From both, the table and the diagram it can be seen that the value of the activity coefficient first decreases as the concentration increases; in many electrolytes it passes through a minimum before rising again. The higher the value of the product of the valences of ions, the greater the drop of the activity coefficient with increasing concentration. In considerably diluted solutions almost equal activity coefficients belong to the electrolytes of the same valence type (e. g. KCl and NaCl, or $ZnCl_2$ and $CaCl_2$); at higher concentration however, individual characteristic properties of various substances manifest themselves.

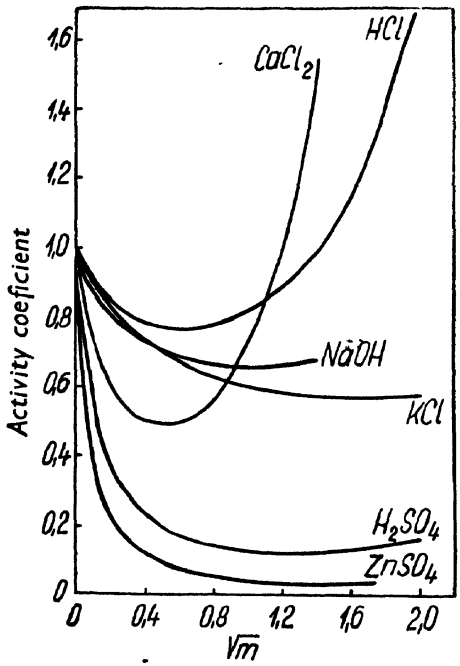


Fig. 6. Dependence of the mean activity coefficient $\gamma_{\pm}$ upon the square root of molality $\sqrt{m}$.

2. Weak Electrolytes

Weak electrolytes are only partly dissociated into ions and their thermodynamic properties in solutions are influenced by electrostatic attractive forces to a much lesser degree, owing to a smaller ionic concentration, than in the case of strong electrolytes. As here it is a case of equilibrium between the dissociated and undissociated parts of the electrolyte, the law of mass action can be applied to the reaction of dissociation.

The problem of equilibrium in the solution of a weak electrolyte, from the point of view of thermodynamics, can be solved as follows: let us assume that e. g. the uni-univalent electrolyte $A\,B$ is dissociated in the solution according to the equation:

$$AB = A^+ + B^-. \qquad \text{(V-42)}$$

If 1 mol of the electrolyte AB becomes split to α gram-ions A^+ and α gram-ions B^-, with the remainder $(1-\alpha)$ of the compound AB undissociated, the so called total mean molal free energy $\bar{G}$ of the dissolved electrolyte is expressed by the sum total of products of the potentials of all components of the electrolyte and the corresponding number of their moles or gram-ions, thus:

$$\bar{G} = \alpha\mu_{A+} + \alpha\mu_{B-} + (1-\alpha)\mu_{AB}.$$

From physico-chemical laws it is obvious that the condition of equilibrium

is expressed by the minimum value of mean molal free energy, which will be ascertained by the differentiation of the last mentioned equation over α and putting $d\bar{G}/d\alpha = 0$:

$$\frac{dG}{d\alpha} = \mu_{A+} + \mu_{B-} - \mu_{AB} = 0.$$

The result reached is in agreement with the equations (V-4) and (V-7), according to which the difference between the free energy of products and that of reactants at equilibrium equals zero:

$$\Delta G = \mu_{A+} + \mu_{B-} - \mu_{AB} = 0. \qquad \text{(V-43)}$$

It is of advantage to choose as the standard state of the undissociated part of the electrolyte its hypothetical unionized state in an ideal solution with the molality $m = 1$ (or molarity $c = 1$), and to consider as the standard state of the dissociated part of the substance its hypothetical completely ionized state in an ideal solution with the ion molality $m_+ = 1$ and $m_- = 1$. If the chemical potential μ°_{AB} corresponds to the first mentioned standard state, and the potential $\mu^\circ_{A+} + \mu^\circ_{B-}$ to the second one, the difference in the standard free energy ΔG° between both states is expressed by the equation:

$$\Delta G^\circ = \mu^\circ_{A+} + \mu^\circ_{B} - \mu^\circ_{AB}.^*) \qquad \text{(V-44)}$$

By subtracting equation (V-43) from the equation (V-44) an equation will be obtained expressing the equilibrium condition:

$$-\Delta G^\circ = (\mu_{A+} - \mu^\circ_{A+}) + (\mu_{B-} - \mu^\circ_{B-}) - (\mu_{AB} - \mu^\circ_{AB}). \qquad \text{(V-45)}$$

Finally by substituting for the individual potential differences the corresponding values of activities from the equation (V-8) the following equation will be obtained:

$$-\Delta G^\circ = RT \ln \frac{a_{A+}\, a_{B-}}{a_{AB}}. \qquad \text{(V-46)}$$

Since at a given temperature the value ΔG° is constant (see equation V-13), the equation (V-43) might also be written in the form:

$$K = e^{-\frac{\Delta G^\circ}{RT}} = \frac{a_{A+}\, a_{B-}}{a_{AB}} \qquad \text{(V-47)}$$

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*) Owing to ignorance of the absolute values of μ°_A, μ°_B and μ°_{AB}, the molal free energies of formation of ions and compounds $\Delta\mu^\circ$ are applied for the computation of ΔG°; $\Delta\mu^\circ$ expresses the difference between the potentials of ions (or compounds) and potentials of elements of which they are composed:

$$\Delta G^\circ = \Delta\mu^\circ_{A+} + \Delta\mu^\circ_{B-} - \Delta\mu^\circ_{AB}.$$

where K is the true thermodynamical dissociation constant of a weak electrolyte. The same expression would be obtained, if the general law of mass action (i. e. the equation (V-14)) would be directly applied for the description of the contemplated equilibrium. The activities in the equation (V-47) could be replaced by the products of concentrations expressed in terms either of molalities or molarities, and the corresponding activity coefficients. In the first instance following equation will be obtained:

$$K_m = \frac{m_{A+}\, m_{B-}}{m_{AB}} \cdot \frac{\gamma_{A+}\, \gamma_{B-}}{\gamma_{AB}}. \qquad \text{(V-48)}$$

The product of the activity coefficients $\gamma_{A+}\ \gamma_{B-}$ may be substituted by the mean activity coefficient $\gamma^2_{\pm m}$ (with the aid of equation (V-36)) and the activity coefficient of the undissociated part of the electrolyte γ_{AB} may be assumed to be nearly unity, since the mutual affecting of the undissociated molecules may be neglected.

The equation (V-48) will, therefore, have this form:

$$K_m = \frac{m_{A+}\, m_{B-}}{m_{AB}} \gamma^2_{\pm m} = K'_m \gamma^2_{\pm m}. \qquad \text{(V-49a)}$$

In this formula K'_m is the dissociation constant expressed solely by the equilibrium concentrations, according to the classical Guldberg-Waage interpretation of the law of mass action. This value is identical with the true thermodynamical dissociation constant K_m in highly diluted solutions only, for which the mean activity coefficient $\gamma_{\pm m}$ very nearly equals unity. In all other solutions K'_m is not a true constant, but it depends on the actual concentration and on the presence of additional electrolytes; therefore, it is called the apparent dissociation constant, in contradistinction of the true dissociation constant. For concentration expressed in terms of molarity, a similar equation is valid·

$$K_c = \frac{c_{A+}\, c_{B-}}{c_{AB}} \gamma^2_{\pm c} = K'_c \gamma^2_{\pm c}. \qquad \text{(V-49b)}$$

By substituting equations (V-41c), $c_{A+} = m_{A+}\rho^\circ$, $c_{B-} = m_{B-}\rho^\circ$ and $c_{AB} = m_{AB}\,\rho^\circ$ into the equation (V-49b) and considering at the same time the equation (V-49a), it can be easily proved that both constants K_m and K_c in diluted solutions are related as shown by the equation

$$K_c = K_m \rho^\circ, \qquad \text{(V-49c)}$$

where ρ° is the density of the solvent.

Pure water may also be considered a weak electrolyte which is very slightly dissociated, according to the equation:

$$H_2O = H^+ + OH^-.*) \qquad \text{(V-50)}$$

Because the activity of undissociated water, owing to its very slight dissociation in diluted solutions, may be regarded as constant, it can be included in the dissociation constant K_m in the following manner:

$$K_m = \frac{a_{H^+}\, a_{OH^-}}{a_{H_2O}}$$

$$K_v = K_m a_{H_2O} = a_{H^+} a_{OH^-} = m_{H^+} m_{OH^-} \gamma^2_{\pm m}. \qquad \text{(V-51)}$$

The constant K_v, which is called the ionic product of water, may be computed from equations (V-44) and (V-46), if partial molal free energies (potentials) of formation of all the reaction components in the corresponding standard states are known. For such standard states we select both the state of a hypothetical ideal solution with molal concentration of hydrogen and hydroxyl ions equalling unity and the state of hypothetical, absolutely undissociated pure water. Since in actual diluted solutions the activity of undissociated water hardly differs from the activity in its standard state, a_{H_2} in the equation (V-51) may be considered as equalling unity so that then $K_m \cong K_v$. The following expression is valid for a temperature of 25° C:

$$\Delta G^\circ = \Delta\mu^\circ_H + \Delta\mu^\circ_{OH^-} - \Delta\mu^\circ_{H_2O} = 0 - 37\,590 + 56\,693 = 19\,103 =$$

$$= -RT\ln K_v = -RT\ln a_{H^+}\, a_{OH^-} = -1364.9 \log a_{H^+} a_{OH^-},$$

from which

$$\log a_{H^+} a_{OH^-} = 14{,}0 \text{ or } a_{H^+} a_{OH^-} = 10^{-14}.**) \qquad \text{(V-52)}$$

In an exactly neutral solution $a_{H^+} = a_{OH^-}$, so that:

$$\log a_{H^+} = \log a_{OH^-} = -7 \quad \text{or} \quad a_{H^+} = a_{OH^-} = 10^{-7}. \qquad \text{(V-53)}$$

From the equation (V-52) it is apparent that the activity of hydrogen ions is inversely proportional to the activity of hydroxyl ions. Following the sugges-

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*) It is more correct to express the dissociation process of water by the equation:

$$H_2O + H_2O = H_3O^+ + OH^-,$$

according to which the products of dissociation are the hydroxonium and hydroxyl ions. According to Brönsted's theory, the hydrogen ion H^+ (or rather the proton) cannot exist independently, but reacts immediately with water, to form the hydroxonium ion. Since, therefore, the so called concentration of hydrogen ions equals the concentration of the hydroxonium ions and due to the very slight dissociation of water the activity of undissociated water is almost unchanged by the proton hydration, the equations (V—51) and (V—52) are in harmony with Bronsted's conception, if the symbol H^+ is indentified with the hydroxonium ion H_3O^+.

**) From accurate electrochemical measurements the ionic product of water will result: $K_v = 1.008 \times 10^{-14}$.

tion of Sörensen the activity of the hydrogen ion is expressed by the negative value of its decadic logarithm and marked by the symbol pH:

$$\mathrm{pH} = -\log a_{\mathrm{H}+}, \text{ so that } a_{\mathrm{H}+} = 10^{-\mathrm{pH}}. \tag{V-54}$$

The activity of hydroxyl ions could be similarly expressed by the definition:

$$\mathrm{pOH} = -\log a_{\mathrm{OH}-} \text{ or } a_{\mathrm{OH}-} = 10^{-\mathrm{pOH}}. \tag{V-55}$$

By substituting the expression (V-54) and (V-55) in the equation (V-52) it follows for the temperature of 25° C:

$$\mathrm{pH} + \mathrm{pOH} = 14. \tag{V-56}$$

In pure water or exactly neutral solutions pH = pOH = 7. In acid aqueous solutions in which $a_{\mathrm{H}+}$ is greater than 10^{-7} the pH is less than 7, in alkaline solutions it is greater than 7.

The ionic product $K_v = a_{\mathrm{H}+}\, a_{\mathrm{OH}-}$ is constant at a given temperature, in so far as pure water or diluted solutions are concerned, since only with such solutions the activity of undissociated water practically equals unity. In pure water or very diluted solutions even the activity coefficient in the equation (V-51) equals very nearly unity, so that the activities of the hydrogen and hydroxyl ions practically equal their concentrations:

$$K_v = a_{\mathrm{H}+}\, a_{\mathrm{OH}-} \cong K'_v = m_{\mathrm{H}+}\, m_{\mathrm{OH}-}.$$

In such diluted solutions the product of ionic concentrations, expressed in terms of molarities, has practically the same value ($K'_v \cong c_{\mathrm{H}+} + c_{\mathrm{OH}-}$), because the density of the solvent is approximately unity.

The product of ionic concentrations has a constant value at given temperatures in pure water or in diluted solutions only. In more concentrated solutions, containing greater amounts of dissolved substances, the values of a_{H_2O} and $\gamma_{\pm m}$ differ considerably from unity. The ionic product K_v can be then calculated from the following equation resulting from the unsimplified equation (V-51):

$$K_m = \frac{a_{\mathrm{H}+}a_{\mathrm{OH}^-}}{a_{\mathrm{H_2O}}} = \frac{m_{\mathrm{H}+}m_{\mathrm{OH}-}}{a_{\mathrm{H_2O}}}\,\gamma^2_{\pm m}$$

$$K'_v = m_{\mathrm{H}+}m_{\mathrm{OH}-} = K_m\,\frac{a_{\mathrm{H_2O}}}{\gamma^2_{\pm m}}.$$

As follows from the last equation the value of the product $m_{\mathrm{H}+}\, m_{\mathrm{OH}-}$ depends, in addition to the equilibrium constant K_m, also upon the activity of undissociated water and upon the activity coefficient as well.

While the activity of the undissociated water $a_{\mathrm{H_2O}}$ becomes less than unity in more concentrated solution, the value of the activity coefficient $\gamma_{\pm m}$ drops at first with increasing concentration and rises again later. These variable factors cause at the given temperature (i. e. at constant K_m) the product

m_{H^+} m_{OH^-} at first to rise with the increasing concentration of the solution, and after reaching a certain maximum, to drop again. For practical calculations this dependence of the ionic product on the composition is usually not taken into consideration with more concentrated solutions, and the value K'_v is even in this case considered as an unvariable constant.

3. Debye-Hückel Theory

As mentioned above, the activity coefficients of diluted solutions could be computed from the Debye-Hückel theory. Since, however, a detailed explanation is beyond the limit of this work, only an explanation of the principles will be given, as well as the results thereof.

The Debye and Hückel theory is based on the assumption that strong electrolytes are completely dissociated in their solutions and the observed deviations from ideal behavior are only caused by electrical forces acting between the ions. Compared with solutions of nonelectrolytes, where the individual molecules are distributed at random, the solutions of strong electrolytes show a tendency to bring about a more regular arrangement in as much as every positive ion is surrounded on an average by a greater number of negative than positive ions. This is due to the electrical forces of attraction and repulsion of charges having the opposite or the same sign respectively, analogously then in the vicinity of each negatively charged ion, positively charged ions rather than the negative ones are agglomerating. In spite of the thermal vibration of ions acting against this regular grouping, the effect of the electrostatic forces will prevail in the end, and round each individual ion, the so called ionic atmosphere will be formed, in which ions of the opposite sign predominate and the resulting charge of which is of the same magnitude, as that of the central ion. The ionic atmosphere which has no fixed boundaries is of maximum density in the close vicinity of the central ion and its field of force gradually ceases to exist with increasing distance. The spatial extension of the ionic atmosphere depends on the concentration of the solution, therefore, the more diluted the solution, the greater the radius of the influence of the central ion, and vice versa.

It follows from this that in the actual (nonideal) solutions the natural tendency of the free moving particles to disperse as much as possible in the given space is counteracted by attractive forces, which tend to concentrate the ions in a volume as small as possible. As every ion is enveloped by the ionic atmosphere having the opposite charge, its electric potential drops below the value it has in a completely free state, i. e. in an infinitely diluted solution in which the mutual electrostatic attraction between the ions of opposite charges is so small, that it may be safely discounted. This drop in the potential of the central ion is the greater, the denser its ionic atmosphere is, or the greater the concentration of the solution. Consequently, a certain electrical work could be gained by transferring the ion from a diluted solution to a concentrated one (or

from an ideal solution to an actual one, of the same concentration), as its electrical potential would diminish by such a transfer. For the opposite process, i. e. for the transfer of the ions from a concentrated solution to a diluted one, electrical work has to be supplied; metaphorically expressed, the ion "is kept" in the more concentrated solution by the ionic atmosphere, which is oppositely charged.

The work gained by the dilution of ideal solutions (the dissolved particles of which are not mutually attracted) depends only on the ratio of the logarithms of the analytical concentrations of the given substance in the final and original solutions. On the other hand, with actual solutions, the work gained on dilution is less than that gained with ideal solutions because the above discussed electrical work, necessary for the separation of ions from their ionic atmosphere has an opposite sign and lowers the work which would be produced by dilution of an ideal solution.

These two kinds of energy are included in the definition of the chemical potential of ions. The difference $W = \mu - \mu^\circ$ indicates the work gained (or consumed) during the transfer of one gram-ion from the state of an actual solution of a concentration c, to an ideal solution with the unity concentration:

$$\mu = \mu^\circ + RT \ln a = \mu^\circ + RT \ln c\gamma = \mu^\circ + RT \ln c + RT \ln\gamma, \quad \text{(V-57)}$$

$$W = \mu - \mu^\circ = RT \ln c + RT \ln \gamma.$$

It follows from the last equation that the net work gained by the dilution of an actual solution of an ion concentration c ($c > 1$) to the state of an ideal solution, with concentration $c = 1$, equals the sum of two constituents. The term of the first constituent, $RT \ln c$, expresses the energy gained by the dilution of the ideal solution and the second one, $RT \ln \gamma$, represents the work, required to overcome the effect of the interionic electrical forces. Since the last mentioned electrical work reduces the value of the work W, which would be gained by the dilution of an ideal solution, the expression $RT \ln \gamma$ must have a negative value, or in other words the activity coefficient of actual solutions $\gamma < 1$. It follows further from this conception that the potential of an electrolyte contained in an actual solution must be lower than the potential of the same substance in an ideal solution.

Debye and Hückel were working out their conceptions mathematically, and found that the mean activity coefficient of a strong electrolyte $A_{r_+}^{z_+} B_{r_-}^{z_-}$ may be expressed by the equation:

$$\log \gamma_{\pm c} = -\frac{Az_+z_- \sqrt{\mu}}{1 + Ba_i\sqrt{\mu}} = -\frac{Az_+z_- \sqrt{0{,}5 \Sigma c_i z_i^2}}{1 + Ba_i \sqrt{0{,}5 \Sigma c_i z_i^2}}, \quad \text{(V-58)}$$

where z_+ and z_- stand for the number of cation and anion charges of the given electrolyte. As both values appear in the equation as a product, it can be seen to what high degree the valence of an electrolyte influences the deviation of its

solution, from the behavior of an ideal solution, (see the decreasing value $\gamma_{\pm c}$); A and B are constants which depend only on the temperature and the dielectric constant of the solvent. As the rising temperature and higher dielectric constant reduce the effect of the interionic forces, the value $\gamma_{\pm c}$ increases.

The constants A and B have for water the following values at certain temperatures:

t	=	18°	25°	38°	100 °C
A	=	0.4992	0.509	0.5186	0.568
$B.10^8$	=	0.3272	0.3286	0.3314	0.342

In the equation (V-58) the quantity μ is of considerable importance, called by Lewis and Randall the ionic strength of the solution, and equals one-half the sum of products of molarities of all the ions present in the solution and the square of their valences:

$$\mu = 0.5 \Sigma c_i z_i^2. \qquad \text{(V-59)}$$

The activity coefficient of a strong electrolyte depends, therefore, on the concentration and valence of both, its own ions and that of all other ions present in the solutions. It follows further from the last two equations that the activity coefficient of a given electrolyte is the same in any solution, if we assume that ionic strength is always the same. According to experimental results, this proposition is more exactly valid with an increased dilution of the solutions.

The quantity a_i, given in equation (V-58) and expressing the average distance between the nearest ions in the solution (i. e. equalling the total of radii of both ions with opposite charges and being within the range of 3—5 $\times$ 10^{-8} cm) determines the specific influence of the electrolytes on the activity coefficient. Because this quantity is not directly measurable, verification of the validity of the Debye - Hückel theory is carried out in such a manner that a value is substituted for a_i, which conforms best with the values of $\gamma_{\pm c}$ obtained by experiments.

As shown in equation (V-58) the $\log \gamma_{\pm c}$ attains its limit value of zero i. e. $\gamma_{\pm c} = 1$, with the concentration c nearly equalling zero. In this respect the equation is in agreement with reality, since the infinitely diluted solution can be regarded as an ideal one. With increasing concentration also the value of $-\log\gamma_{\pm i}$ increases ($\gamma_{\pm c}$ becomes less than unity); in a sufficiently concentrated solution the quantity $-\log \gamma_{\pm c}$ should, according to the equation, come closer to the second limit value Az_+z_-/Ba_i. This is not actually so, as the activity coefficient, according to experimental results, with increased concentration at first diminishes, until it reaches its minimum and then it again increases. The reason for the inaccuracy of the Debye-Hückel theory for higher concentrations is not only due to a series of simplifications carried out during deduction of the formula (V-58) to overcome mathematical difficulties, but also to the fact that only the existence of attractive interionic forces were taken into consideration and other phenomena were neglected, for instance the association of

ions, the change of the dielectric constant of the solvent by the effect of the charged ions present and the bonds between ions and molecules of the solvent, which are manifested to a higher degree at higher concentrations of the solutions.

When calculating the activity coefficient from the Debye-Hückel equation the average value 3×10^{-8} cm might be substituted for a_i into the equation (V-58) for solutions with concentration not exceeding $c = 0.1$ with uni-univalent electrolytes ($c = 0.05$ with bi-univalent ones). Because in aqueous solutions at 25° C $A = 0.509$ and $B = 0.329 \times 10^{-8}$, the Debye -Hückel equation for the mentioned type of solutions has quite a simple form:

$$\log \gamma_{\pm c} = - \frac{0.509 \sqrt{c}}{1 + \sqrt{c}}. \tag{V-60}$$

In still more diluted solutions of uni-univalent electrolytes, up to the maximum molarity about $c = 0.01$ (with electrolytes of a higher valence type this limit is, of course, still lower) the term $Ba_i \sqrt{\mu}$ may be neglected against unity, so that the equation (V-58) is simplified to the so called Debye-Hückel limiting law:

$$\log \gamma_{\pm c} = - Az_+z_- \sqrt{\mu} \tag{V-61}$$

which for electrolytes of the 1—1 type at the temperature of 25° C takes the form:

$$\log \gamma_{\pm c} = - 0.509 \sqrt{c}, \text{ or } \gamma_{\pm c} \cong 1 - 1.15 \sqrt{c}. \tag{V-62}$$

As can be seen from these equations the specific nature of individual ions is not expressed any more in very diluted solutions and the activity coefficient is determined solely by the ionic strength and the valence type of the electrolyte. Assuming the solutions to be properly diluted, the activity coefficients of electrolytes of the same valence type are identical in all solutions of the same ionic strength.

The original form of the Debye-Hückel equation permits the calculation of the mean activity coefficients of strong electrolytes in solutions defined by their molarity c. Should the value of this coefficient be expressed by molality, which is more advantageous in electrochemistry, it will be possible in the case of a sufficiently diluted solution to substitute into the equation (V-58) for $\gamma_{+c} = \gamma_{\pm m}$ (see V-41c) and for molarities of all ions the product of their molalities and the density of the solvent $c_i \cong m_i \rho^\circ$, so that:

$$\log \gamma_{+m} = - \frac{A \sqrt{\rho^\circ} z_+z_- \sqrt{0.5 \Sigma m_i z_i^2}}{1 + B \sqrt{\rho^\circ} a_i \sqrt{0.5 \Sigma m_i z_i^2}}. \tag{V-63}$$

As far as aqueous solutions are concerned, where the solvent density ρ° does not practically differ from 1, we can see from the equation just stated that the

Debye-Hückel equation is valid in unchanged form for concentrations expressed both by molality and molarity.

Although Debye and Hückel worked out their theory to solve the problem of strong, completely dissociated electrolytes, the results may be applied to weak and transition electrolytes as well, if the actual ionic concentration is substituted in the equation for ionic strength. With strong electrolytes, which are completely dissociated, it is possible to substitute in the term $\frac{1}{2}\Sigma c_i z_i^2$ directly the analytical concentration of the substance, but with weak electrolytes their dissociation degree α has to be considered. For example with uni-

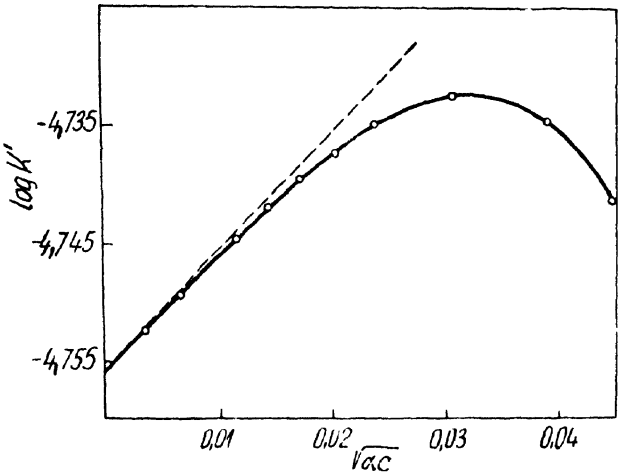


Fig. 7. Determination of the dissociation constant of acetic acid from the conductivity measurements of its solution.

univalent electrolyte the actual concentration of each ion is given by the product αc, where c is the analytical concentration of the compound applied. If we now apply the Debye-Hückel limiting law to sufficiently diluted solutions, the activity coefficient of the dissociated fraction of the uni-univalent electrolyte, according to equation (V-62) at 25° C will equal:

$$\log \gamma_{\pm c} = -0.509\sqrt{\alpha c}. \qquad \text{(V-64)}$$

By substituting this term into the equation (V-49b) the following equation will ensue:

$$\log K'_c = \log K_c + 1.018\sqrt{\alpha c} \qquad \text{(V-65)}$$

expressing the difference sought between the true thermodynamic dissociation constant K_c and the apparent dissociation constant K'_c in relation to the dissociation degree of a weak electrolyte at various concentrations of solution.

According to this equation the relation of log K'_c to the term $\sqrt{\alpha c}$ should be graphically expressed as a straight line, the slope of which equals $a = 1.018$ and the intercept on the axis of ordinates $b = \log K_c$ (for $c = 0$).

Such a a diagram valid for diluted acetic acid is shown in Fig. 7. The required values of the dissociation degree α were found by measurement of conductivity of solutions with varying molarity c and the apparent dissociation constant K'_c was computed according to the formula:

$$K'_c = \frac{c_{A+}\, c_{B-}}{c_{AB}} = \frac{\alpha^2 c}{1 - \alpha}.$$

As can be seen from the diagram the tangent of the curve is in strict agreement with the equation (V-65) (see the dashed straight line); on the other hand the individual points of the curve coincide with the dashed line only up to the ionic concentration about $\alpha c = 1.5 \times 10^{-4}$; with higher concentrations the full curve deviates from the dashed straight line, proving that the Debye-Hückel limiting law is not valid any longer.

The dissociation constants of weak acids are determined, in the described manner, according to conductivity measurements. From the diagram of the dissociation of acetic acid it follows that the intercept on the axis of ordinates $\log K'_c = \log K_c = -4.756$, from which the true dissociation constant $K_c = 1.75 \cdot 10^{-5}$ at 25° C.

VI. GALVANIC CELLS

Galvanic cells are systems combined in a suitable manner in which the chemical or other form of potential energy is converted into electrical energy. The cells consist of one or more electrolytic conductors in which two electrodes are suspended; by connecting the electrodes with a metallic conductor the electric current will flow through the system.

For the production of electrical energy in galvanic cells processes are utilized, which are caused by electron interchange between the substances concerned. Because the electrons cannot exist in a free state in greater concentration, each electronic reaction consists of two partial processes. One of them is oxidation, during which the electrons are released by a certain substance, and the other is reduction during which another substance consumes the electrons released in the first process. While in chemical reaction both these processes take place inseparably and closely beside each other, the typical characteristic of galvanic cells is that both oxidation and reduction take place in two different spatially separated spots, i. e. on both electrodes. The electrons released during the process of oxidation in a galvanic cell are not delivered directly to the process of reduction, but only by means of the external electric circuit. At the same time the passage of electrons through the external conductor gives rise to electric current, the energy of which could be used for the performance of work.

A. MEASUREMENTS OF ELECTROMOTIVE FORCES OF GALVANIC CELLS

The maximum of energy obtainable during the galvanic cell operation is expressed by the product of the quantity of electricity passed through the cell and the voltage across the electrodes, called the electromotive force of a cell *(EMF)*.

It has been already explained during the interpretation of the Faraday Law, how the amount of electricity is determined. The second component necessary for determining the magnitude of electrical energy, i. e. the voltage, can be measured by a voltmeter connected to the galvanic cell terminals. This method, however, is not accurate, because through the measuring circuit a certain current passes, which always causes the reading on the voltmeter to be somewhat lower than the true electromotive force of the cell. The reason for this is the internal resistance of the cell, which must be overcome by a certain potential difference and polarization phenomena, which act against the electromotive force of the cell and so lower its value.

If the electromotive forces of all the cells are to be determined precisely they must be measured when no current is passing through them. For this purpose

the well known Poggendorf's compensation method is applied on the principle of which a number of variously adapted potentiometers is based.

As shown in diagram Fig. 8. the principle of measuring consists of switching variable voltage from a lead plate storage battery AK (with a higher voltage than the measured cell) by means of a potentiometer AB with a sliding contact D against the electromotive force under examination X, until the galvanometer G, or other current indicating device will not show any deflection. At this moment the EMF of the cell X just equals the potential difference across the

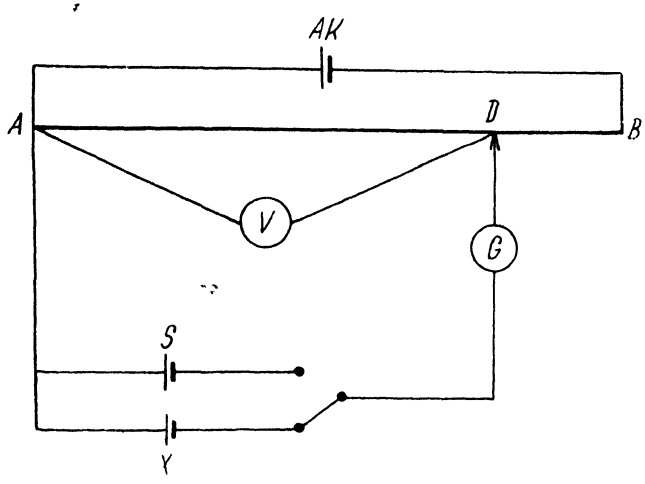


Fig. 8. Measuring of electromotive forces.

section AD of the measuring wire, measurable directly by a voltmeter V, with a high internal resistance.

The examined electromotive force E_x could be determined more accurately by assessing first the length of the measuring wire AD_x, which has been used for the compensation of the EMF of the cell X by the opposing voltage of the storage battery AK. The measured cell X is then replaced by a standard cell S with precisely known electromotive force E_S and the length of the measuring wire AD_S is found, at which the galvanometer shows the zero deflection. Both EMF's E_x and E_s are then related to the lengths AD_x and AD_s, thus

$$E_x : E_s = AD_x : AD_s$$

or

$$E_x = E_s \frac{AD_x}{AD_s}.$$

Recently voltage has been measured by an electronic voltmeter; the main

advantage of this is that practically no current is required for indication, so that the resistance of the measured cell can be of considerable value.

The Weston cell is the most suitable standard cell for measuring electromotive forces because of its excellent reproducibility; it is shown in diagrammatical form in Fig. 9.

An H shaped glass container has electrodes at the bottom of the lower arms connected to the external wires by sealed-in platinum wires. The negative electrode is of cadmium amalgam containing 12.5 % cadmium, while the positive electrode is formed by mercury with a layer of paste, which consists of mercurous sulphate, dispersed mercury and small crystals of cadmium sulphate. Both electrodes are covered by fine ground crystals of cadmium sulphate $CdSO_4 \cdot {}^8/_3\, H_2O$ and the remaining part of the container is filled with a saturated solution of the same salt.

The reaction taking place in the current producing cell is expressed by the equation:

$$Cd\ (amalgam) + Hg_2SO_4 + {}^8/_3\, H_2O = CdSO_4 \cdot {}^8/_3\, H_2O + 2\, Hg.$$

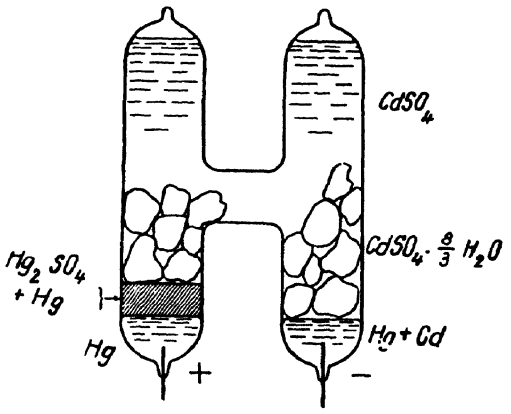


Fig. 9. Weston Standard Cell.

When the potential on the cell terminals is higher than the electromotive force of the cell the process proceeds in a reverse direction. The surplus of solid salts (Hg_2SO_4 and $CdSO_4 \cdot {}^8/_3\, H_2O$) ensures that the solutions at both electrodes are always saturated, so that the electrode potentials are constant at a constant temperature. The dependence on the temperature of the *EMF* of the described Weston cell is expressed by the equation:

$$E = 1.0183 - 4.06 \times 10^{-5}\,(t - 20) - 9.5 \times 10^{-7}\,(t - 20)^2.$$

B. REVERSIBLE AND IRREVERSIBLE CELLS

When applying thermodynamic laws to the so called reversible galvanic cells their *EMF* can be deduced mathematically from characteristics of the system. Reversible cells are those in which the direction of reactions proceeding in them can be reversed when a voltage of an opposite direction is applied to the electrodes, which is only higher by an infinitesimal value then the *EMF* of the system proper.

An example of a reversible cell is the well known Daniell cell. This consists of a zinc electrode immersed into a solution of zinc sulphate and a copper electrode in a solution of cupric sulphate; both solutions are in the same vessel but separated by a diaphragm (a porous partition), which prevents the liquids mixing, but allows the migration of the ions. As long as the electrodes are not connected no chemical reaction takes place in the cell. After connecting the electrodes the zinc electrode starts to dissolve and the metallic copper from the solution starts to be deposited at the cathode according to the equation:

$$Zn + Cu^{++} = Zn^{++} + Cu,$$

and at the same time the electric current will start to flow through the circuit.

After compensating the *EMF* of the cell in Poggendorf's connection by an external voltage exactly identical in magnitude, but opposite in direction, reaction in the cell will cease. When we reduce the external compensating voltage by an infinitesimally small value (e. g. by one millionth of a volt), the cell will start to produce a small amount of electrical energy (the reaction proceeds in accordance with the above mentioned equation from left to right). If, however, the external *EMF* were increased by an equally infinitesimal value, the cell would start to take in a certain small amount of electrical energy from the external current source, which would be expended in the course of the reaction proceeding in an opposite direction (i. e. for the copper solution and deposition of zinc):

$$Zn^{++} + Cu = Zn + Cu^{++}.$$

Such a system, therefore, could be reversed into the original state by supplying energy from an external source after having done a certain amount of work as a galvanic cell. Theoretically, exactly the same amount of work must be expended as was obtained when the system worked as a cell. To fulfill, this assumption it would be necessary to discharge and charge the cell by an infinitesimally small current, during an infinitely long time, so that conditions by which the *EMF* of the system is determined would remain unchanged. When an actually higher current flows through the cell, concentration differences arise within the cell due to the slow diffusion of ions, eventually, other polarization phenomena may occur; thus the equilibrium of the system is disturbed and the discharging potential of the cell is lower and the charging potential higher than the open circuit potential.

With irreversible cells the energy obtained by discharging the cell and required for charging is not equal, even when those processes are realized at an infinitesimally small current. As an example of such a system the Volta cell can be quoted, in which the zinc and copper electrodes are dipped in a solution of diluted sulphuric acid. During generation of electric energy in this cell, the zinc dissolves in the acid and the hydrogen is evolved at the copper electrode:

$$Zn + 2\,H^{+} = Zn^{++} + H_2.$$

Contrary to reversible cells, this reaction proceeds, though at a very limited rate, even when the electrodes are not connected and no current is flowing through the cell. If its *EMF* is compensated in a potentiometric connection by an equal potential of opposite direction, the zinc dissolution continues. Should the compensating potential exceed the *EMF* of the cell, the above mentioned reaction will not proceed in the opposite direction but a new process appears instead, during which the copper is dissolved and the hydrogen is evolved on the zinc electrode:

$$Cu + 2\,H^+ = Cu^{++} + H_2.$$

On reversing the current direction the system does not return to the original state.

C. ELECTROMOTIVE FORCE OF REVERSIBLE CELLS

As already mentioned, the *EMF* of a reversibly operating cell may be calcu lated from the thermodynamic properties of the system, i. e. from the equivalency between the maximum electric work which can be obtained when the cell is operating at constant temperature and pressure, and the change in free energy accompanying the corresponding chemical reaction.

If n gram-equivalents of substances are consumed during an electrochemical reaction the quantity of electricity nF coulombs will flow through the cell, and will be transfered to a potential level which is higher by E volts. The product of both quantities indicates the maximum electrical work W_{max}, which may be gained during this process from the chemical energy, thus:

$$W_{max} = nFE \text{ joules} = 23\,066\,nE \text{ cal}^*)$$

where E is the reversible equilibrium voltage of a galvanic cell. Further, if ΔG signifies the change in free energy of the system during a reaction its equivalence with the electrical work performed may be expressed by this equation, which is an important connecting link between thermodynamics and electrochemistry:

$$W_{max} = nFE = -\Delta G = 23\,066\,nE \text{ cal}^{**}) \qquad \text{(VI-1)}$$

This equation in not only of considerable value in electrochemistry proper, when calculating the reversible potential of galvanic cells, but is also of great service in thermodynamics for ascertaining various thermodynamic constants.

In the reversible Daniell cell the reaction of two gramequivalents of zinc is accompanied by the free energy loss $\Delta G = -51{,}063$ cal at 25 °C, if the activity of the Zn^{++} and Cu^{++} ions in both solutions equals unity. The equilibrium

*) Since 1 joule = 0,239 cal, F joules = 96,500 × 0,239 = 23066 cal.

**) The equation (VI-1), of course, is not valid for irreversible cells, where a part of the free energy will be lost through conversion into thermal energy.

voltage of the cell E, operating under the same conditions for which the above mentioned change of free energy of the corresponding reaction is valid, equals, therefore, according to the equation (VI-1):

$$E = -\frac{\Delta G}{23\,066\,n} = -\frac{(-51\,063)}{2\,.\,23\,066} = 1.107 \text{ V.}^{*})$$

The galvanic cell operating at constant temperature either absorbs heat from the surroundings, or evolves it; this absorbed or evolved heat is called latent heat. It follows from the thermodynamics laws that the sum total of free energy change ΔG, converted in a reversible cell quantitatively into the electrical work and of latent heat Q_{rev}**) equals the enthalpy change ΔH:

$$\Delta G + Q_{rev} = \Delta H$$

or

$$-W_{max} = \Delta G = \Delta H - Q_{rev} = -23\,066\,nE \text{ cal} \qquad \text{(VI-2)}$$

$$E = \frac{-\Delta H + Q_{rev}}{23\,066\,n} = \frac{Q_p + Q_{rev}}{23\,066\,n}\,. \qquad \text{(VI-2a)}$$

The enthalpy change ΔH, being an important thermodynamic function of state, is identical with the negative value of the heat of reaction (Q_p), when the reaction proceeds under constant pressure in a purely chemical way (e. g. in a calorimeter), the $\Delta H = -Q_p$. The quantity ΔH expresses, therefore, the value of the total energy set free or absorbed during a reaction proceeding under constant pressure.

In a Daniell cell at the given concentrations ($a_{Zn^{++}} = 1$, $a_{Cu^{++}} = 1$) there is

$$\Delta G = -51063 \text{ cal and } \Delta H = -51\,300 \text{ cal,}$$

$$\text{thus: } Q_{rev} = \Delta H - \Delta G = -51300 - (-51\,063) = -237 \text{ cal.}$$

It follows from this result, that during the reversible and isothermal course of reaction in the Daniell cell the total chemical energy ΔH, evolved under constant pressure in the course of reaction is not utilized for current generation, but a certain part of it (237 cal) is transfered to the surroundings in the form of heat. With other cells, on the contrary, the free energy change ΔG is greater than the change in enthalpy ΔH; therefore, a certain amount of heat Q_{rev} is obsorbed from the surroundings in the course of isothermal and reversible operation of such systems.

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*) In the given example ($a_{Zn^{++}} = 1$, $a_{Cu^{++}} = 1$) the cell is operating under standard conditions, the calculated electromotive force E, therefore, represents the standard electromotive force $E°$.

**) According to the thermodynamic laws the latent heat is determined by the product of the absolute temperature and the entropy change ΔS, relating to the reaction:

$$Q_{rev} = T\,\Delta S.$$

Because the heat Q_{rev} is usually of a lower order than the value ΔH, it can be disregarded when no high accuracy is required ($Q_{rev.} \cong 0$), so that the formula (VI-2a) will read:

$$E \cong \frac{Q_p}{23066\, n}. \qquad \text{(VI-3)}$$

This equation, called the Thomson formula, is given mainly in old textbooks on electrochemistry as an approximate equation which expresses the relation between the *EMF* of a cell and the heat of reaction. As will be seen from the explanation of electrolysis below, the same formula may be also used for a rough estimate of the decomposition voltage of a compound, if no other data, except the reaction heat, are available. It is worth mentioning that the Thompson formula is precisely valid only with such systems the electromotive force of which does not change with temperature.

The electromotive force of a given cell apart from temperature and pressure also depends on the concentration of the active substances in the system. This dependence for a common reaction

$$aA + bB + \ldots = lL + mM + \ldots$$

will be found on starting with the familiar equation (see formula (V-11)) which expresses the relationship between the change in free energy ΔG, the change in standard free energy ΔG° and the activities:

$$\Delta G = \Delta G^\circ + RT \ln \frac{(a_L)^l\,(a_M)^m \ldots}{(a_A)^a\,(a_B)^b \ldots}. \qquad \text{(VI-4)}$$

In this equation we substitute for ΔG and ΔG° the equivalent values of the electrical work from (VI-1)

$$-(\Delta G) = nFE$$
$$-(\Delta G^\circ) = nFE^\circ$$

wherein the voltage E° corresponding to the change ΔG°, is called the standard reversible potential of the galvanic cell. Thus a very important equation, deduced first by *Nernst*, is formulated and it expresses the dependence of the cell *EMF* on the concentration of active substances:

$$E = E^\circ - \frac{RT}{nF} \ln \frac{(a_L)^l\,(a_M)^m \ldots}{(a_A)^a\,(a_B)^b \ldots}. \qquad \text{(VI-5)}$$

In this equation E signifies the electromotive force of the cell in which the reacting substances have activities a_A, a_B.... On the other hand, E° is the electromotive force of the cell, if all the reaction components were in the standard state, i. e. if the activity of each component would equal unity.

When transferring in the second term of the equation (VI-5) the natural

logarithm into a decadic one and substituting for $R = 8.315$ joule/°K, mol and $F = 96.500$ C, the following value will be obtained for the constant:

$$2.3026 \frac{RT}{F} = \frac{2.3026 \cdot 8.315\, T}{96\,500} = 1.984 \cdot 10^{-4}\, T$$

having for various temperatures the following values:

°C	°K	$\frac{2.3026\, RT}{F}$
0	273.15	0.05419
10	283.15	0.05618
20	293.15	0.05816
25	298.15	0.05915
30	303.15	0.06014

By using the equation (VI-5) for the Daniell cell, where at a temperature of 25 °C $E^\circ = 1.107$ V, the formula for the calculation of the equilibrium *EMF* for an electrolyte of any composition will be then obtained:

$$E = 1.107 - \frac{0{,}05915}{2} \log \frac{a_{Zn^{++}}}{a_{Cu^{++}}} =$$

$$= 1.107 - \frac{0{,}05915}{2} \log \frac{m_{Zn^{++}} \gamma_{Zn^{++}}}{m_{Cu^{++}} \gamma_{Cu^{++}}}.$$

During the operation of the Daniell cell the concentration (activity) of zinc ions is increased and the activity of the cupric ions is decreased. In this way its electromotive force diminishes, until finally it will drop to zero. By substituting this condition ($E = 0$) into the already mentioned Nernst's equation the value of the ratio $a_{Zn^{++}}/a_{Cu^{++}}$ can be calculated at which the cell is completely inactive. The activity ratio mentioned at the same time expresses the equilibrium constant of the reaction taking place in the Daniell cell:

$$\log \frac{a_{Zn^{++}}}{a_{Cu^{++}}} = \frac{2 \cdot 1{,}107}{0{,}05915} \cong 37, \quad \text{or} \quad a_{Cu^{++}} \cong \frac{a_{Zn^{++}}}{10^{37}}.$$

When the activity of the cupric ions will drop to a value 10^{37} times smaller than the activity of zinc ions, the cell will cease to generate current. The same can be said about the concentration of cupric salt, because at such a great difference of activity the activity coefficients can be disregarded. The same equilibrium will be obtained by the precipitation of copper from a solution of its salts by metallic zinc, if the process of precipitation is carried out by a chemical method, i. e. by copper displacement (cementation).

D. DENOTATION OF THE ELECTROMOTIVE FORCE

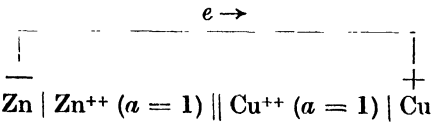
It was stated in Chapter V. that spontaneous reactions occurring at constant temperature and pressure are characterized by the negative sign of the change in free energy $\Delta G < 0$, non-spontaneous reactions by the positive sign of that change $\Delta G > 0$ and the process in a state of equilibrium by the zero value of that change $\Delta G = 0$.

The galvanic cell is a system in which a certain reaction proceeds spontaneously i. e. $\Delta G < 0$. When substituting this condition into the equation (VI-1), it is apparent that the EMF of a galvanic cell must always have a positive sign. On the contrary, reactions in which the ΔG has a positive sign, hence the corresponding EMF has a negative sign, cannot proceed spontaneously but must be carried out in an electrolyzer and the energy required must be supplied from an external source.

To make absolutely clear in which direction the electrochemical reaction proceeds and which is the polarity of the electrodes, diagrams of electrode systems are represented according to the following rule: The electrode at which oxidation takes place is written always on the left side of the diagram, while the electrode at which reduction occurs is on the right side; the electromotive force of the cell has then a positive sign.

Oxidation in the galvanic cells takes place at that electrode which emits electrons into the external circuit and which has a negative charge. On the other hand reduction takes place at the positively charged electrode where the electrons are consumed.

According to this principle, the diagram of the Daniell cell in which zinc forms the negative and copper the positive electrode is as follows



Following to this diagram the electrons move in the external electric circuit from the left to the right.

In systems where ΔG has a positive sign and thus the corresponding EMF a negative one (i. e. with electrolyzers) reduction takes place at the electrode into which the electrons enter from the current source and so charge it negatively. From the second electrode at which the oxidation takes place the electrons are led to the current source; so the positive pole is formed at the electrode. Were e. g. the Daniell cell connected with the source of electric current and the electrolytical process took place in it, i. e. the copper were dissolved and zinc deposited from the solution, it would be necessary according to the above mentioned rule to write the diagram in the reverse order and to assign to the electromotive force the negative sign to emphasize that the process is not

a spontaneous one, but requires an input of electric energy with the minimum voltage of 1.107 V:



$$Cu \mid Cu^{++}\ (a = 1) \parallel Zn^{++}\ (a = 1) \mid Zn;\ E^{\circ} = -1.107\ V.$$

E. THE ORIGIN OF ELECTRODE POTENTIALS ACCORDING TO THE NERNST CONCEPTION

Up to now the galvanic cell was described as a system, and little attention has been paid to processes occurring at the individual electrodes.

The total potential difference across the terminals of a cell is the sum of the potential differences, arising at the boundaries of two different phases. The most important boundary is that one between the electrode and the electrolyte. At the junction of two solutions of the same electrolyte but of different concentrations or solutions containing different electrolytes a potential difference will also arise, i. e. the so called liquid junction potential or diffusion potential which is, however, rather small (it will be dealt with in more detail later on).

In the cell diagrams the boundary between the electrode and the electrolyte, where the potential difference arises, is marked by a single vertical line (e. g. $Zn \mid Zn^{++}$). The line dividing two electrolytes (e. g. $Zn^{++} \mid Cu^{++}$) expresses the existence of the liquid junction potential added to the electrode potentials. When this liquid junction potential is eliminated (e. g. by a salt bridge, see below), so that it can be disregarded, a double line is written instead of a single one ($Zn^{++} \parallel Cu^{++}$).

The origin of potentials at the interface between the electrode and the electrolyte can be explained by the older but intuitive conception of *Nernst*. By this conception, the electrode producing cations (metal or hydrogen dissolved in platinum) in contact with an electrolyte shows a tendency to dissolve and form positively charged ions, while the electrons thus freed are left on the electrode and give it a negative charge. This tendency is caused by electrolytic solution pressure which is rather a measure of the cations ability to leave the metal lattice and enter the solution. The magnitude of the solution pressure is influenced also by solvatation forces which facilitate the transfer of the metal cations from the crystal lattice to the electrolyte. According to Nernst, the osmotic pressure of the metal ions already present in the electrolyte, acts against solution pressure and on the contrary it tries to transfer the ions to the electrode and deposit them on the surface of the crystal lattice. In this way the electrode becomes positively charged and the solution with a surplus of anions becomes negatively charged. The sign of the resulting electrode charge and its magnitude depend on the ratio of both forces and this in turn depends on the nature and composition of both the electrode and the electrolyte.

With base metals (e. g. alkali metals, iron, zinc etc.) in which the valence electrons in the atoms are more loosely bound the electrolytic solution pressure

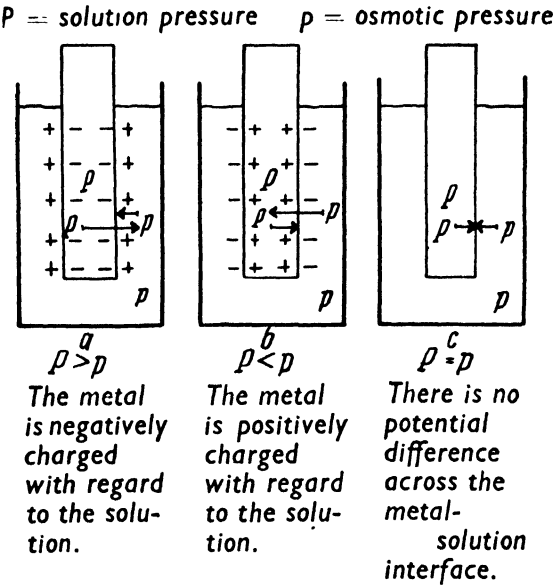


Fig. 10. Nernst's Explanation of the origin of electrode potentials.

P exceeds the osmotic pressure p of their ions in solution; therefore the electrode has a negative charge with respect to the solution (see Fig. 10, diagram *a*). It is quite the opposite in the case of noble metals (Cu, Ag, Pt etc.) which acquire a positive charge in not too diluted solutions of their ions (diagram *b*). In systems, where the solution pressure of the metal is just counterbalanced by the osmotic pressure of its ions in the solution, no potential difference between the electrode and the electrolyte will arise (diagram *c*).

The origin of the electric current in the Daniell cell, an important representative of a galvanic cell, will now be dealt with in detail. A zinc electrode exerts

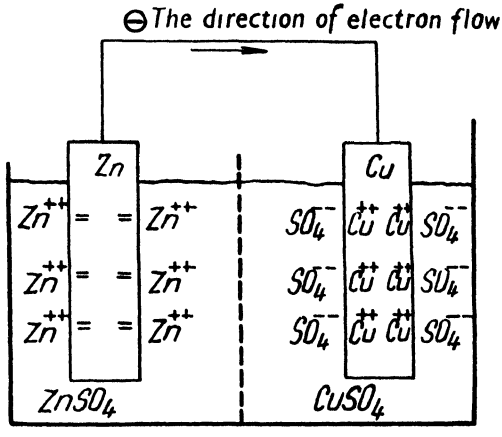


Fig. 11. A diagram of the Daniell cell.

greater solution pressure than a copper electrode (see Fig. 11.). Therefore, a small quantity of zinc will be brought into the solution in the form of ions and will leave behind at the same time two electrons for each ion formed. The solution will thus become positively charged while the metal will be negatively charged. As a result of the great electrostatic force the opposite charges produced are held very close to the interface between the electrode and electrolyte and form an electric double layer with a certain potential difference across it. This double layer can be regarded as a parallel plate condenser, the depth of which is of molecular dimensions. In this instance the electrons are at the zinc electrode surface and the zinc cations on the interface between the double layer and the solution. If the electrodes are not connected, the equilibrium at the electrode is rapidly established and a further dissolution of the zinc is prevented by both, the osmotic pressure of the zinc ions already present in the solution and by the above described electrical double layer, which inhibits further transfer of positive ions to the solution. In the state of equilibrium both these forces are exactly counterbalanced by the solution pressure. The change in ion concentration in the electrolyte, which is connected with the forming of the double layer is, of course, almost undetectable and cannot be determined analytically. The potential difference across the electrical double layer, the gradient of which is very steep near the electrode and rapidly diminishes in the direction of the solution, expresses the absolute electrode potential; the magnitude of this potential is, however, not directly measurable.

On the other (copper) electrode the electrolytic solution pressure is lower than the osmotic pressure of the cations in the solution and therefore cupric ions from the solution are deposited, thus giving the metal a positive charge, while the solution becomes negative due to the excess of anions (SO_4^{--}). Both kinds of charges Cu^{++} and SO_4^{--} are attracted and form again the electrical double layer. In this case, however, the double layer has an opposite effect than at the zinc electrode as it facilitates the transfer of the cupric ions from the electrode to the solution and prevents them being transferred in the opposite direction. Equilibrium will be attained, when the electrostatic forces of the double layer and the solution pressure of copper together will counterbalance the osmotic pressure of the cupric ions in the solution.

Up to now a cell without any current flow was described. When both electrodes are connected by a metallic conductor, the electrons will start to flow through the external electric circuit from the zinc to the copper electrode. The impulse for this phenomenon is given by the copper electrode which draws the electrons lacking from the zinc electrode where they are in abundance. By this transfer of electrons the original equilibrium at the electrodes will be disturbed. This will result in endeavouring the zinc electrode to compensate for the loss of electrons by an increased production of them, accompanied by the production of new zinc cations from the electrode substance:

$$Zn = Zn^{++} + 2e.$$

During the current flow through a Daniell cell the zinc electrode dissolves and at the same time at the second electrode a tendency is shown to renew the original equilibrium, disturbed by the transfer of electrons, by a process during which the system Cu | Cu^{++} is consuming these new electrons. This process consists of a discharge of the cupric cations, which results in the deposition of metallic copper on the positive electrode:

$$Cu^{++} + 2\,e = Cu.$$

The dissolution of zinc at one electrode and the deposition of copper at the other is, therefore, an inseparably connected process, which is caused by the flow of electrons in the external electric circuit from the zinc to the copper electrode.

The origin of the potential difference on electrodes which emit anions to the solution and which become positively charged against the solution can be explained similarly. Thus, e. g. chlorine dissolved in a platinum electrode shows a tendency to pass to an ionic state by accepting the electrons (from the platinum):

$$Cl_2 + 2\,e = 2\,Cl^-,$$

or the oxygen tends to form under similar conditions in aqueous solutions hydroxyl ions:

$$\tfrac{1}{2}\,O_2 + H_2O + 2\,e = 2\,OH^-.$$

Such electrodes differ from metalic ones only in the fact that the solution due to the negative charge of the ions formed gets negatively charged against the electrode, when the electrolytic solution pressure of the element is greater than the osmotic pressure of its anions in the solution.

F. SINGLE ELECTRODE POTENTIALS

Without taking into account the existence of the liquid junction potential, the process in the galvanic cell can be imagined to consist of two partial processes which take place at the positive and negative electrodes. Both electrode processes may then be regarded as completely independent excepting the fact that the quantities of the substances reacting at both electrodes are given by Faraday's law. It is, therefore, possible to study the separate reactions independently on the so called half cells, or elements, which may be suitably combined to form any desired cell.

Thus, e. g. the process which occurs in a Daniell cell can be divided into the process of oxidation taking place at the negative electrode,

$$Zn = Zn^{++} + 2\,e,$$

and the process of reduction at the positive electrode

$$Cu^{++} + 2\,e = Cu.$$

Both these reactions have their own characteristic potentials which depend only on the nature of each separate half cell. The electromotive force of the

cell, composed of two of such elements, then equals to the algebraic total of the potentials at both electrodes. It must be carefully considered in this calculation which electrode forms the positive pole and which the negative, or at which electrode the oxidation and at which the reduction process takes place. When denoting the oxidation potential of the process taking place at the negative electrode I of a cell by ε_I, and the reduction potential of the positive electrode II by the symbol π_{II} (in order to differentiate it from the oxidation potential), the *EMF* of the cell is given by their total:

$$E = \varepsilon_I + \pi_{II}. \tag{VI-6a}$$

The respective oxidation and reduction potentials of the same half cell are of the same magnitude; differing, however, by the sign ($\varepsilon = -\pi$). It is thus possible to compute the resulting *EMF* of a galvanic cell also from the equations:

$$E = \varepsilon_I - \varepsilon_{II}, \tag{VI-6b}$$

$$E = -\pi_I + \pi_{II}. \tag{VI-6c}$$

G. CALCULATION OF THE ELECTRODE POTENTIALS

The equation (VI-5) gives the Nernst formula valid for the relation between the *EMF* of a cell and the composition of a system in which the overall reaction proceeds:

$$aA + bB = lL + mM$$

We assume that the substance A is oxidized to L and the substance B reduced to M. Let as now divide the overall reaction into oxidation and reduction phases.

When expressing the oxidation process, proceeding at the negative electrode, by the equation:

$$aA = lL + ne,$$

the corresponding half cell will have the oxidation potential:

$$\varepsilon_I = \varepsilon_I^\circ - \frac{RT}{nF} \cdot \ln \frac{(a_L)^l}{(a_A)^a}. \tag{VI-7}$$

Analogously the reduction reaction at the positive electrode:

$$bB + ne = mM$$

is determined by the reduction potential:

$$\pi_{II} = \pi_{II}^\circ - \frac{RT}{nF} \ln \frac{(a_M)^m}{(a_B)^b}. \tag{VI-8}$$

The sum of equations (VI-7) and (VI-8) will give the following expression:

$$\varepsilon_I + \pi_{II} = \varepsilon_I^\circ + \pi_{II}^\circ - \frac{RT}{nF} \ln \frac{(a_L)^l\,(a_M)^m}{(a_A)^a\,(a_B)^b}$$

which must be identical with the equation (VI-5), expressing the relation between E and E° valid for the overall process. By comparing both equations, hence:

$$E = \varepsilon_I + \pi_{II} \qquad \text{(VI-9)}$$

and

$$E^\circ = \varepsilon_I^\circ + \pi_{II}^\circ.$$

In these formulae ε_I° and π_{II}° indicate the standard electrode potentials which are established, when all the half cell components are in their standard state and have activities equalling unity. The relation between the standard oxidation and standard reduction potentials of the same element is exactly the same as those formed with other potentials, i. e. for example $\varepsilon_I^\circ = -\pi_I^\circ$.

It follows from equation (VI-7) and (VI-8) that the reversible electrode potential in an arbitrary state can be calculated, when its standard potential (ε° or π°) and the activity of each component taking part in the reaction at the electrode is known.

H. STANDARD POTENTIALS

To express the absolute values of single potentials is made difficult by the fact that the absolute zero electrode is not known, in respect of which other elements could be measured. It is, therefore, necessary to be satisfied with comparative values. These will be obtained by referring each potential to an exactly defined arbitrary standard electrode the potential of which is conventionally taken as zero. Such comparative potential values, of course, do not prevent the calculation of the *EMF's* of cells composed of two elements because in such instance the "zero" electrode potential proper appears in the corresponding equation twice; once with a positive, and once with the negative sign, so being annuled in the result.

Today, generally the standard hydrogen electrode is taken as the zero electrode. It is defined by a reversible system

$$H_2\ (p = 1\ \text{atm.}) \mid H^+\ (a_{H^+} = 1)$$

where the gaseous hydrogen possesing the pressure of 1 atm. is in contact with a solution containing hydrogen ions with an activity equalling unity.*) Ac-

*) Such a solution is e. g. one with an exact concentration of 1,18 N – HCl; the 1 N – HCl solution does not give the standard electrode since the hydrogen ion activity in it is only $a_{H^+} = 0{,}811$. On defining the standard hydrogen electrode the nature of the acid and its concentration need not be stated. This is justified by the fact, that for calculations of potentials we need the definition of such an electrode only, and its design is less important.

Until the importance of the activity was recognized, an electrode saturated with hydrogen under pressure of 1 atm. in a solution of 2 N – H_2SO_4 was, according to Nernst, called the normal hydrogen electrode. In such an electrolyte, where normal hydrogen ions concentration was assumed, according to conductivity measurements, the activity does not equal unity, but is approximately three times smaller due to the great ionic strength of sulphuric acid.

cording to a convention the potential of an electrode so determined equals zero at any temperature, thus $\varepsilon^{\circ}_{Pt,H_2 \mid H^+} = \pi^{\circ}_{H^+ \mid H_2,Pt} = 0$. The other electrode potentials, referred to the zero potential of the standard hydrogen electrode, are called the potentials on the hydrogen scale.

As stated in the previous chapter, to determine the reversible potential of any electrode in an arbitrary state, it is first of all necessary to know its standard potential. The required values of these potentials, stated in terms of the hydrogen scale and valid for a temperature of 25 °C, are tabulated. Such data do not express the absolute potentials but the electromotive force of the combination of the given half cell and the standard hydrogen electrode. This fact must be remembered, when making calculations based on these potentials.

The values of the electrode standard potentials were obtained by measuring the *EMF's* of suitably arranged cells at varying concentrations and by extrapolating the found values into a state of infinitely diluted solutions in which the activity coefficients of electromotively active substances equal unity. To determine standard potentials is very laborious and requires considerable care. A detailed description of the working method and the method of results evaluation is beyond the limits of this book; it is, therefore, necessary to refer to the pertinent technical literature.

According to nowadays usual practice, the above-mentioned tables contain the standard oxidation potentials of electrodes at 25 °C. Potentials of electrodes at which in combination with a standard hydrogen electrode a spontaneous oxidation process occurs, are taken as positive (e. g. $\varepsilon^{\circ}_{Zn \mid Zn^{++}} = +0.762$ V). On the other hand potentials of electrodes at which under identical conditions the process of reduction takes place, are taken as negative (e. g. $\varepsilon^{\circ}_{Pt,Cl_2 \mid Cl^-} = -1.358$ V). The electrode with the highest oxidation potential is tabulated first and all the others are grouped subsequently below, in order of their diminishing potentials. The electrode with the lowest oxidation potential, i. e. with the highest reduction potential is at the bottom of the table (see Table 9.).

Each substance, which can be readily oxidized and which shows a high oxidation potential, is at the same time a powerful reducing agent. Therefore, metals at the upper end of the standard potential series, called also the voltage series, are powerful reducing agents; their reducing power gradually diminishes in the direction of hydrogen. Substances with negative oxidation potentials are difficult to oxidize, but easy to reduce. Such substances are reduced more readily, i. e. are the more powerful oxidizing agents, the nearer they are to the bottom of the table.

Further, it follows from the table that the reduced form of any metal or ion in the standard state (a = 1) is capable reducing an oxidized form of any metal or ion in the standard state with a less positive standard oxidation potential. Thus e. g. with the element $Pt \mid Sn^{++}, Sn^{++++}$ is $\varepsilon^{\circ} = -0.15$ V and with the half cell $Pt \mid Hg_2^{++}, Hg^{++}$ is $\varepsilon^{\circ} = -0.910$ V. The reduced form of the first half

Tab. 9. Standard oxidation electrode potentials (25 °C)

Electrode	Reaction at the electrode	ε° (volts)
Li|Li$^+$	$Li = Li^+ + e$	+ 3,025
K|K$^+$	$K = K^+ + e$	+ 2,923
Ca|Ca^{++}	$\frac{1}{2}Ca = \frac{1}{2}\,Ca^{++} + e$	+ 2,763
Na|Na$^+$	$Na = Na^+ + e$	+ 2,713
Zn|Zn^{++}	$\frac{1}{2}Zn = \frac{1}{2}Zn^{++} + e$	+ 0,762
Fe|Fe^{++}	$\frac{1}{2}Fe = \frac{1}{2}Fe^{++} + e$	+ 0,440
Pt|Cr^{++}, Cr^{+++}	$Cr^{++} = Cr^{+++} + e$	+ 0,410
Cd|Cd^{++}	$\frac{1}{2}\,Cd = \frac{1}{2}\,Cd^{++} + e$	+ 0,402
Pb, PbSO$_4$|SO$_4^{--}$	$\frac{1}{2}\,Pb + \frac{1}{2}\,SO_4^{--} = \frac{1}{2}\,PbSO_4 + e$	+ 0,355
Tl|Tl$^+$	$Tl = Tl^+ + e$	+ 0,336
Pb, PbBr$_2$|Br$^-$	$\frac{1}{2}\,Pb + Br^- = \frac{1}{2}PbBr_2 + e$	+ 0,280
Co|Co^{++}	$\frac{1}{2}\,Co = \frac{1}{2}\,Co^{++} + e$	+ 0,277
Ni|Ni^{++}	$\frac{1}{2}\,Ni = \frac{1}{2}\,Ni^{++} + e$	+ 0,250
Ag, AgJ|J$^-$	$Ag + J^- = AgJ + e$	+ 0,151
Sn|Sn^{++}	$\frac{1}{2}\,Sn = \frac{1}{2}\,Sn^{++} + e$	+ 0,140
Pb|Pb^{++}	$\frac{1}{2}\,Pb = \frac{1}{2}\,Pb^{++} + e$	+ 0,126
Pt, D$_2$|D$^+$	$\frac{1}{2}\,D_2 = D^+ + e$	+ 0,0034
Pt, H$_2$|H$^+$	$\frac{1}{2}\,H_2 = H^+ + e$	± 0,0000
Pt|Ti^{+++}, Ti^{++++}	$Ti^{+++} = Ti^{++++} + e$	− 0,04
Ag, AgBr|Br$^-$	$Ag + Br^- = AgBr + e$	− 0,073
Hg, Hg$_2$Br$_2$|Br$^-$	$Hg + Br^- = \frac{1}{2}\,Hg_2Br_2 + e$	− 0,139
Pt|Sn^{++}, Sn^{++++}	$\frac{1}{2}\,Sn^{++} = \frac{1}{2}\,Sn^{++++} + e$	− 0,15
Pt|Cu$^+$, Cu^{++}	$Cu^+ = Cu^{++} + e$	− 0,167
Ag, AgCl|Cl$^-$	$Ag + Cl^- = AgCl + e$	− 0,2223
Hg, Hg$_2$Cl$_2$|Cl$^-$	$Hg + Cl^- = \frac{1}{2}\,Hg_2Cl_2 + e$	− 0,268
Cu|Cu^{++}	$\frac{1}{2}\,Cu = \frac{1}{2}\,Cu^{++} + e$	− 0,345
Pt, O$_2$|OH$^-$	$OH^- = \frac{1}{4}\,O_2 + \frac{1}{2}\,H_2O + e$	− 0,401
Pt, J$_2$|J$^-$	$J^- = \frac{1}{2}\,J_2 + e$	− 0,535
Hg, Hg$_2$SO$_4$|SO$_4^{--}$	$Hg + \frac{1}{2}\,SO_4^{--} = \frac{1}{2}\,Hg_2SO_4 + e$	− 0,614
Pt|Fe^{++}, Fe^{+++}	$Fe^{++} = Fe^{+++} + e$	− 0,771
Hg|Hg$_2^{++}$	$Hg = \frac{1}{2}\,Hg_2^{++} + e$	− 0,7988
Ag|Ag$^+$	$Ag = Ag^+ + e$	- 0,799
Pt|Hg$_2^{++}$, Hg^{++}	$\frac{1}{2}\,Hg_2^{++} = Hg^{++} + e$	− 0,910
Pt, Br$_2$|Br$^-$	$Br^- = \frac{1}{2}\,Br_2 + e$	− 1,0654
Pt|Tl$^+$, Tl^{+++}	$\frac{1}{2}\,Tl^+ = \frac{1}{2}\,Tl^{+++} + e$	− 1,250
Pt, Cl$_2$|Cl$^-$	$Cl^- = \frac{1}{2}\,Cl_2 + e$	− 1,358
Pb, PbO$_2$|Pb^{++}	$\frac{1}{2}\,Pb^{++} + H_2O = \frac{1}{2}\,PbO_2 + 2H^+ + e$	− 1,456
Pt|Ce^{+++}, Ce^{++++}	$Ce^{+++} = Ce^{++++} + e$	− 1,61
Pt|Co^{++}, Co^{+++}	$Co^{++} = Co^{+++} + e$	− 1,84

cell, i. e. Sn^{++}, will, therefore, reduce the oxidized form of the active component of the second half cell, i. e. Hg^{++}, according to the equation:

$$\tfrac{1}{2}\,Sn^{++} + Hg^{++} = \tfrac{1}{2}\,Sn^{++++} + \tfrac{1}{2}\,Hg_2^{++}.$$

The degree to which the reaction can proceed is the greater the further apart both substances are in the standard potential series. Thus e. g. from the potential values of the elements $Zn \mid Zn^{++}$ and $Pt \mid Co^{++}, Co^{+++}$ it follows that the equilibrium constant of the reaction $\tfrac{1}{2}\,Zn + Co^{+++} = Co^{++} + \tfrac{1}{2}\,Zn^{++}$ at 25 °C is approximately $K = 10^{44}$, which means that the salt of the trivalent cobalt is reduced by zinc almost completely. The equilibrium constant $K = 6.4$ will belong on the other hand to the reaction $Fe + Cd^{++} = Cd + Fe^{++}$; this comparatively small value shows a considerable amount of cadmium ions remaining in a state of equilibrium and not reduced.

It is natural that the possibility of ionic reaction can be reliably predicted from the standard potential series only when the activities of all components taking part in the reaction equal unity. At other activities the mutual relations of substances in the potential series can be changed. There is a second limitation, namely, no retardation of the reactions by various foreign phenomena (e. g. by overvoltage or mechanical pasivity of the surface, due to the existence of oxide films).

It is apparent from the table that the half cell represented by the symbol "electrode — ions" means that an oxidation process takes place there, so that its potential ε has the sign given in the table. On the other hand the order of the symbols representing a half cell at which the reduction process proceeds is the opposite, i. e. "ions — electrode", and the corresponding potential π has an opposite sign than that given in the table.*)

It has already been mentioned that it is important to remember in which direction the reaction proceeds in half cells, when calculating the ***EMF*** of a cell from the potentials of the half cells, forming that cell, and to draw a correct distinction between the quantities ε° and π°. Thus e. g. the standard oxidation potential of the element $Pt \mid Sn^{++}, Sn^{++++}$ has a negative value $\varepsilon^\circ = -0.15$ V. This means that at the electrode in combination with the

*) To distinguish clearly the oxidation and reduction potentials the symbols ε and π are provided with symbolic suffixes expressing symbolically the kind of electrode reaction. If in this suffix the electrode is written on the left side the oxidation process takes place; if the reduction process takes place, the electrode is written on the right side of the suffix. The application of such symbols will be illustrated by a few examples:

Kind of reaction:	Writing of potential:
$Zn = Zn^{++} + 2e$ (oxidation)	$\varepsilon_{Zn} \mid Zn^{++}$
$2\,OH^- = H_2O + \tfrac{1}{2}\,O_2 + 2e$ (oxidation)	$\varepsilon_{Pt,O_2} \mid OH^-$
$Cu^{++} + 2e = Cu$ (reduction)	$\pi_{Cu^{++}} \mid Cu$
$Cl_2 + 2e = 2\,Cl^-$ (reduction)	$\pi_{Cl^-} \mid Cl_2,Pt$

standard hydrogen electrode there will be a positive pole and a reduction process will take place at the reduction potential $\pi^\circ = 0.15$ V. In the cell which is schematically represented:

$$\mathrm{Pt,H_2 \mid H^+}(a = 1) \parallel \mathrm{Sn^{++}}\ (a = 1),\ \mathrm{Sn^{++++}}\ (a = 1) \mid \mathrm{Pt};$$
$$E^\circ = 0 + 0{,}15 = 0{,}15\ \mathrm{V}$$

a spontaneous reaction takes place:

$$\mathrm{H_2} + \mathrm{Sn^{++++}} = 2\ \mathrm{H^+} + \mathrm{Sn^{++}}.$$

If, however, the same electrode is combined to form a cell with an electrode which has a more negative oxidation potential, e. g. such as the half cell $\mathrm{Pt} \mid \mathrm{Hg_2^{++}}$, $\mathrm{Hg^{++}}$ ($\varepsilon^\circ = -0.91$, or else $\pi^\circ = 0.91$ V), its function is reversed:

$$\mathrm{Pt} \mid \mathrm{Sn^{++}}\ (a = 1),\ \mathrm{Sn^{++++}}\ (a = 1) \parallel \mathrm{Hg_2^{++}}\ (a = 1),\ \mathrm{Hg^{++}}\ (a = 1) \mid \mathrm{Pt},$$
$$E^\circ = -0{,}15 + 0{,}91 = 0{,}75\ \mathrm{V},$$
$$\tfrac{1}{2}\ \mathrm{Sn^{++}} + \mathrm{Hg^{++}} = \tfrac{1}{2}\ \mathrm{Sn^{++++}} + \tfrac{1}{2}\ \mathrm{Hg_2^{++}}.$$

Similarly at the cadmium electrode oxidation will take place at the oxidation potential $\varepsilon^\circ = 0.402$ V, when combining with the copper electrode, which due to its nobler nature acts in this system as a positive electrode with a reduction potential $\pi^\circ = 0.345$ V:

$$\mathrm{Cd} \mid \mathrm{Cd^{++}}\ (a = 1) \parallel \mathrm{Cu^{++}}\ (a = 1) \mid \mathrm{Cu},$$
$$E^\circ = 0{,}402 + 0{,}345 = 0{,}747\ \mathrm{V},$$
$$\mathrm{Cd} + \mathrm{Cu^{++}} = \mathrm{Cd^{++}} + \mathrm{Cu}.$$

When replacing the copper electrode by the much less noble electrode of zinc ($\varepsilon^\circ = 0.762$ V), at the cadmium electrode ($\pi^\circ = -0.402$ V) a reduction proces will proceed:

$$\mathrm{Zn} \mid \mathrm{Zn^{++}}\ (a = 1) \parallel \mathrm{Cd^{++}}\ (a = 1) \mid \mathrm{Cd},$$
$$E^\circ = 0{,}762 + (-0{,}402) = 0{,}360\ \mathrm{V},$$
$$\mathrm{Zn} + \mathrm{Cd^{++}} - \mathrm{Zn^{++}} + \mathrm{Cd}.$$

1. ELECTRODES

Electrodes or half-cells, used in electrochemistry can be divided into following groups:

1. Electrodes of the type: metal in contact with its ions.
2. Electrodes of the type: amalgam in contact with its ions.
3. Nonmetal electrodes in contact with their ions.
4. Gas electrodes.
5. Electrodes of the type: metal in contact with an insoluble salt or oxide.
6. Redox (oxidation — reduction) electrodes.

1. Electrodes of the type: metal in contact with its ions

Electrodes of this type are usually called "electrodes of the first class". They are represented by a metal electrode immersed into a solution of a salt with the same cation. At such an electrode the equilibrium is formed according to the equation:

$$M = M^{+n} + ne$$

to which, as follows from the general equation (VI-7), this equilibrium oxidation potential will belong:

$$\varepsilon_{M \mid M^{+n}} = \varepsilon^{\circ}_{M \mid M^{+n}} - \frac{RT}{nF} \ln \frac{a_{M^{+n}}}{a_M} . \qquad \text{(VI-10)}$$

Since in a system metal — ions, the metal activity is $a_M = 1$, the last equation will be simplified to

$$\varepsilon_{M \mid M^{+n}} = \varepsilon^{\circ}_{M \mid M^{+n}} - \frac{RT}{nF} \ln a_{M^{+n}} = \varepsilon^{\circ}_{M \mid M^{+n}} - \frac{1.984 \cdot 10^{-4} T}{n} - \log a_{M^{+n}}. \qquad \text{(VI-11)}$$

The potential of such an electrode is, therefore, determined by the activity of its own ions in the electrolyte; such an electrode is said to be reversible with respect to its own cations. It is well known that the activity a_{M+n} is expressed by the product of the molality (or molarity) and the activity coefficient of the respective ion. Since, however, the activity coefficients of individual ions are not known, they are being replaced by the mean activity coefficients $\gamma \pm$. In sufficiently diluted solutions it is possible to substitute in the formula (VI-11) directly the concentrations for activities, since the activity coefficients in this instance would very nearly equal unity.

It follows from the equation (VI-11) that the oxidation potential of the metal electrode becomes more positive with decreasing activity (concentration) of the solution. This means that the negative charge at the electrode is increased and the electrode acquires the characteristic properties of a less noble metal On the other hand, with an increased concentration the oxidation potential decreases. This means that the electrode shows a decreasing tendency to emit ions and its negative charge is diminishing so that the metal behaves almost like a more noble metal. The electrode, immersed into a saturated solution of its own salt has comparatively the most negative potential.

2. Electrodes of the type: amalgam in contact with its ions

An amalgam is an alloy of mercury with another metal. The mercury is electrochemically inactive, if the metal dissolved is a baser metal. The mercury in this case acts only as a solvent, decreasing the activity of dissolved metal. This lowering of activity is of great use with metals of high reactivity (e. g. with

the alkali metals) which in pure state cannot be used for electrochemical measurements in aqueous solutions. The amalgam electrodes have a further advantage, that equilibria are established with them more rapidly and reproducibly, than with pure metals.

As is apparent from the next equation which expresses the state of equilibrium at the electrode

$$M\mathrm{Hg}_x = M^{+n} + x\mathrm{Hg} + ne,$$

and from the general equation (VI-7), the potential of an amalgam electrode depends both on the metal activity in the amalgam and on the activity of its ions in the solution

$$\varepsilon_{M\mathrm{Hg}_x \mid M^{+n}} = \varepsilon_{M\mathrm{Hg}_x \mid M^{+n}} - \frac{RT}{nF} \ln \frac{a_{M^{+n}}}{a_{M\mathrm{Hg}_x}}. \qquad \text{(VI-12)}$$

The formula is valid if the amalgamated metal is monoatomic.

3. Nonmetal electrodes in contact with their ions

To prepare electrodes both metals and nonmetals can be applied. Iodine in a solid state in contact with iodide solution can, for example, become an electrode reversible with respect to the iodide ions. When making such an electrode the iodine is placed into a glass vessel and the iodide solution poured over it; current connection is made by a platinum wire, which is in contact with the iodine and acts as an indifferent electrode. Equilibrium at the electrode is attained according to the formula:

$$J^- = \tfrac{1}{2} J_{2(s)} + e,$$

to which belongs the equilibrium oxidation potential:

$$\varepsilon_{\mathrm{Pt,J_2} \mid J^-} = \varepsilon^\circ_{\mathrm{Pt,J_2} \mid J^-} + \frac{RT}{F} \ln a_{J^-}. \qquad \text{(VI-13)}$$

In this equation $\varepsilon^\circ_{\mathrm{Pt,J_2} \mid J^-}$ represents the standard oxidation potential of the iodine electrode ($\varepsilon^\circ_{\mathrm{Pt,J_2} \mid J^-} = -0.535$ V) and a_{J^-} the activity of iodide ions in the solution. The negative value of this potential means that in combination with a hydrogen electrode a spontaneous reduction process will take place at the iodine electrode during which iodine will pass into the solution in ionic form.

4. Gas electrodes

Electrodes of this type (i. e. hydrogen, chlorine and oxygen electrodes) consist of a platinum wire or foil, immersed into the electrolyte contained in a glass or quartz vessel. Gas bubbles through the solution, so that the surface of the electrode becomes constantly saturated with it. Owing to its pressure the gas will partially dissolve in the platinum and behave then as a metal

electrode, emitting its ions into the surrounding electrolyte. Platinum which hardly forms any ions, as it has a very slight electrolytic solution pressure, is only a conductor of electrons, which are produced or consumed during the electrochemical reaction of gases. To obtain a rapidly reproducible equilibrium between the gas and its ions, the platinum electrode is coated with platinum black.

Among gas electrodes, the hydrogen electrode is widely used for electrochemical measurements, particularly for pH measurements. One form of hydrogen electrode is shown in Fig. 12. The glass vessel *A* is half filled with the electrolyte, which contains hydrogen ions of an unknown concentration and a platinum electrode *E* coated with platinum black is partly immersed in it. The hydrogen is lead to the bottom of the vessel by an outside pipe, bubbles through the solution and leaves the vessel (through the water seal) *B*. By means of a side tube *T* the hydrogen electrode is connected with another electrode of a known potential (e. g. a calomel electrode), usually by means of a salt bridge (see below).

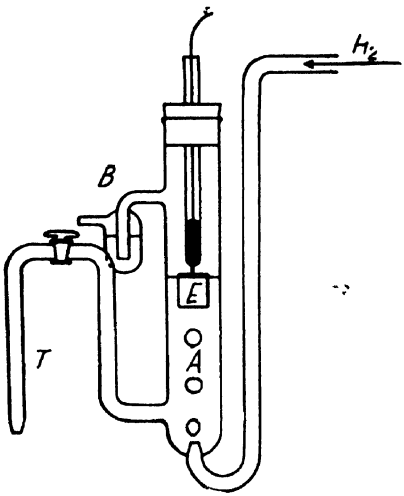


Fig. 12. The hydrogen electrode.

When making exact measurements the water vapour content in the hydrogen has to be taken into consideration and the measured *EMF* value corrected to the partial pressure of hydrogen of 1 atm. In addition the oxygen has to be completely removed from the hydrogen applied and no substances which could be reduced by hydrogen in the presence of platinum must be present in the solution (e. g. ferric ions, nitrate, chromate or unsaturated organic compounds). Substances which act as poisons on the platinum electrode are also detrimental and must be removed (certain organic compounds, especially sulphur and cyanide compounds and surface active agents).

Hydrogen, which is dissolved and absorbed in the platinum black is capable of emitting its ions into the solution. On the surface of the platinum electrode the reversible equilibrium between the hydrogen and its ions in the solution is attained according to the equation:

$$\tfrac{1}{2}\,H_2(p_{H_2}) = H^+\,(a_{H^+}) + e.$$

The activity of the gaseous hydrogen can be substituted at lower and medium pressures by its partial pressure, expressed in atm. and then the following equation is valid for the equilibrium potential:

$$\varepsilon_{Pt,H_2 \mid H^+} = \varepsilon^{\circ}_{Pt,H_2 \mid H^+} - \frac{RT}{F} \ln \frac{a_{H^+}}{p_{H_2}^{\frac{1}{2}}}. \qquad \text{(VI-14)}$$

The hydrogen electrode potential depends, therefore, on the activity of the hydrogen ions in the solution as well as on the pressure of the gaseous hydrogen. It can be seen in the formula, that the oxidation potential becomes more positive at constant hydrogen pressure with decreasing activity of hydrogen ions (e. g. by reducing the activity of ions to one tenth at a temperature of 25 °C, the oxidation potential increases by 59 millivolts). The potential also becomes more positive at a constant concentration of hydrogen ions if the gaseous hydrogen pressure is increased (at a hundred times greater pressure the potential will rise by 59 millivolts).

Since the standard potential of the hydrogen electrode $\varepsilon^{\circ}_{H_2}$ is considered at any temperature at zero value, the equation (VI-14) can be written:

$$\varepsilon_{Pt,H_2 \mid H^+} = -\frac{RT}{F} \ln a_{H^+} + \frac{RT}{2F} \ln p_{H_2}.$$

When working with hydrogen at a pressure of 1 atm., $\ln p_{H_2} = 0$ and the hydrogen electrode potential only depends on the activity of the hydrogen ions in the solution:

$$\varepsilon_{Pt,H_2 \mid H^+} = -\frac{RT}{F} \ln a_{H^+}. \qquad \text{(VI-15)}$$

This equation is of great importance in electrochemistry because by it the activity of hydrogen ions or the pH of the solution can be computed from the measured *EMF* of a suitably combined cell.

A chlorine electrode shows a similar behavior as a hydrogen electrode because its potential is a function of the pressure of the gas surrounding the electrode and of the activity of chloride ions in the solution. The oxidation potential will be calculated by the already known method from the corresponding equilibrium

$$Cl^-(a_{Cl^-}) = \tfrac{1}{2}\, Cl_2(p_{Cl_2}) + e,$$

and from the general equation (VI-7)

$$\varepsilon_{Pt,Cl_2 \mid Cl^-} = \varepsilon^{\circ}_{Pt,Cl_2 \mid Cl^-} - \frac{RT}{F} \ln \frac{p_{Cl_2}^{\frac{1}{2}}}{a_{Cl^-}}. \qquad \text{(VI-16)}$$

In the cell formed by combining with the hydrogen electrode the chlorine electrode emits anions into the solution and is charged positively. This means that a spontaneous reduction process takes place:

$$\tfrac{1}{2}\, Cl_2(p_{Cl_2}) + e = Cl^-(a_{Cl^-}),$$

characterized by the reduction potential:

$$\pi_{Cl^- \mid Cl_2, Pt} = \pi^\circ_{Cl^- \mid Cl_2, Pt} - \frac{RT}{F} \ln \frac{a_{Cl^-}}{p^{\frac{1}{2}}_{Cl_2}}.$$

Chlorine and hydrogen electrodes under suitable conditions behave in a reversible manner. On the contrary no suitable material has yet been found for the oxygen electrode which would rapidly catalyze the attainment of equilibrium between oxygen and hydroxyl ions, according to the equation:

$$OH^-(a_{OH^-}) = {}^1/_4\, O_2(p_{O_2}) + \tfrac{1}{2}\, H_2O + e.$$

The oxidation potential corresponding to this equation can be expressed by the following equation:

$$\varepsilon_{Pt, O_2 \mid OH^-} = \varepsilon^\circ_{Pt, O_2 \mid OH^-} - \frac{RT}{F} \ln \frac{p^{\frac{1}{4}}_{O_2}}{a_{OH^-}}. \qquad \text{(VI-17)}$$

As the oxygen electrode does not operate in a reversible manner, it is not possible to measure the value of ε° directly. To determine the value of ε°, method of calculation has been applied, using the known values of the free energy changes of the reactions:

$$H_2(1\text{ atm}) + \tfrac{1}{2}\, O_2(1\text{ atm}) = H_2O_{(l)};\ \Delta G^\circ_{298,1} = -56\,693\text{ cal},$$
$$2\, H_2O_{(l)} = 2\, H^+ + 2OH^-;\qquad \Delta G^\circ_{298,1} = +38\,206\text{ cal}.$$

The total of both equations is:

$$H_2(1\text{ atm}) + \tfrac{1}{2}\, O_2\,(1\text{ atm}) + H_2O_{(l)} = 2\, H^+ + 2\, OH^-$$
$$\Delta G^\circ_{298,1} = -18\,487\text{ cal}.$$

Now let us imagine that the process represented by the latter equation is carried out in a hypothetical galvanic cell composed according to this scheme:

$$Pt, H_2(1\text{ atm}) \mid H^+(a_{H^+} = 1) \parallel OH^-(a_{OH^-} = 1) \mid O_2\,(1\text{ atm}), Pt.$$

The theoretical reversible potential of this cell can be computed according to formula (VI-1):

$$E^\circ = -\frac{\Delta G^\circ}{23\,066\, n} = \frac{18\,487}{2\,.\,23\,066} = 0.401\text{ V}.$$

The reaction in the mentioned cell can be divided into an oxidation process proceeding at the negative electrode:

$$H_2(1\text{ atm}) = 2\, H^+ (a_{H^+} = 1) + 2\, e;\ \varepsilon^\circ_{Pt, H_2 \mid H^+} = 0,$$

and the reduction process at the positive electrode:

$$\tfrac{1}{2}\, O_2\,(1\text{ atm}) + H_2O_{(l)} + 2\, e = 2\, OH^-\,(a_{OH^-} = 1);\ \pi^\circ_{OH^- \mid O_2, Pt}.$$

According to equation (VI-9) the sum total of both potentials gives the ***EMF*** of the considered cell:

$$E^\circ = 0.401 = \varepsilon^\circ_{Pt,\,H_2\,|\,H^+} + \pi^\circ_{OH^-\,|\,O_2,\,Pt} = 0 + \pi^\circ_{OH^-\,|\,O_2,\,Pt},$$

from which follows the standard reduction potential of the oxygen electrode:

$$\pi^\circ_{OH^-\,|\,O_2,\,Pt} = 0.401 \text{ V}$$

and its oxidation potential as:

$$\varepsilon^\circ_{Pt,\,O_2\,|\,OH^-} = -0.401 \text{ V}.$$

5. Electrodes of the type: metal in contact with an insoluble salt or oxide

Electrodes of this type are sometimes called electrodes of the second class and are applied in electrochemistry as the reference electrodes for measuring unknown potentials. They are formed by a metal in contact with its insoluble salt, which is immersed into a solution of a soluble electrolyte with the

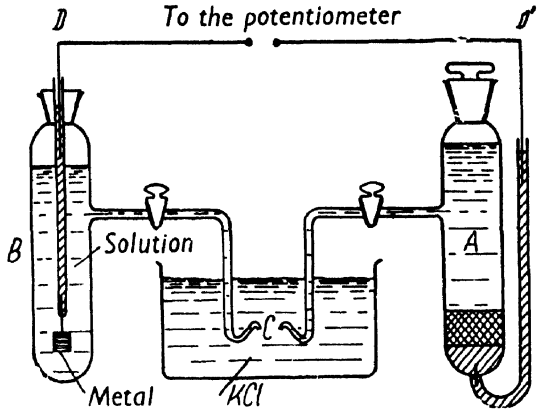


Fig. 13. Measurement of electrode potentials.

same anion as that of the insoluble salt. Calomel, silver-silver chloride (called argento-chloride), mercurosulphate and other electrodes are among this group.

Compared with the hydrogen electrode reference electrodes are more advantageous as they are easy to prepare, easier to work with, and give perfectly reproducible potentials; their electrolytes generally have so small liquid junction potentials that they can be disregarded. Since their potentials, compared with the standard hydrogen electrode are exactly known, the in-

vestigated potential of the unknown half cell on the hydrogen scale might be obtained by simple calculation of the measured *EMF*.

When measuring an unknown electrode potential the half cell under examination $M \mid M^+$ is combined with a reference electrode (e. g. a calomel one) in the manner illustrated in Fig. 13. In this figure *A* is the calomel electrode, *B* the element to be measured and *C* the salt bridge, which forms the electric connection between *A* and *B* and eliminates at the same time the liquid junction potential. The potential between *A* and *B* is measured in the normal way by Poggendorf's potentiometric method.

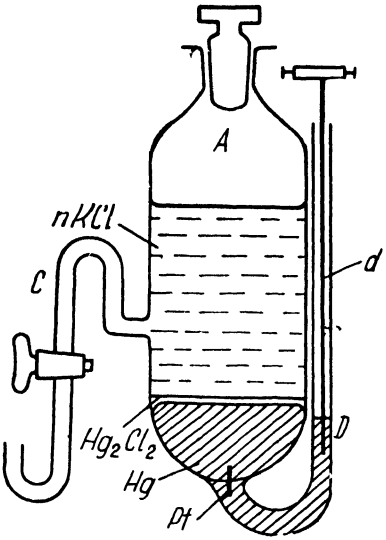


Fig. 14. The Calomel Electrode.

When the electromotive force of the system under examination equals *E* and at the reference electrode the reduction process takes place, the sought for oxidation potential ε of the half cell investigated can be calculated from equation (VI-6a):

$$\varepsilon = E - \pi_{ref},$$

where the π_{ref} is the reduction potential of the reference electrode, referred to the standard hydrogen electrode.

The calomel electrode, which is best known of all, has usually the form illustrated in Fig. 14. The glass vessel *A*, properly closed with a rubber plug, carries the tube *C* equipped with a cock. The tube is filled with an appropriate solution of potassium chloride thus forming the liquid junction with the other electrode.

Electrical connection is made by a platinum wire sealed into the narrow bottom part of the vessel. To the bottom of the vessel the arm *D* is welded which is partly filled with mercury. An amalgamated wire is immersed into the mercury and connected to the terminal.

A small quantity of pure mercury is placed at the bottom of the vessel and covered with a layer of a paste consisting of mercurous chloride, mercury and potassium chloride solution of an appropriate concentration. Above the paste the vessel is filled with a potassium chloride solution saturated with mercurous chloride. According to the concentration of the potassium chloride solution (0,1 *N* — KCl, 1 *N* — KCl or saturated solution of KCl) the decinormal, normal or saturated calomel electrodes are distinguished.

The function of calomel electrode may be explained as follows. The positive current enters e. g. the solution from mercury. The mercury is then dissolved and renders mercurous ions, according to the equation:

$$\text{a)}\ Hg_{(l)} = \tfrac{1}{2}\, Hg_2^{++} + e.$$

As the electrolyte has previously been saturated with mercurous chloride the value of the solubility product of the mentioned salt will be transgressed by the entry of the ions Hg_2^{++} into the solution. In order to maintain equilibrium the production of mercurous ions is, therefore, immediately followed by the reaction:

$$b)\ \tfrac{1}{2}\ Hg_2^{++} + Cl^- = \tfrac{1}{2}\ Hg_2Cl_{2(s)}\ ,$$

during which the mercurous chloride will be separated in a quantity exceeding the concentration corresponding to its solubility product. By addition of the two equations, a) and b), an equation will be obtained, which expresses the overall oxidation process at the electrode:

$$c)\ Hg_{(l)} + Cl^- = \tfrac{1}{2}\ Hg_2Cl_{2(s)} + e.$$

When the current flows in the opposite direction reaction will proceed from right to left and the mercurous ions will become reduced at the cathode rendering metallic mercury.

The potential difference between the mercury and the solution in which the activity of mercurous ions is $a_{Hg_2^{++}}$, is expressed with regard to equation a) by the formula:

$$\varepsilon_{Hg\ |\ Hg_2^{++}} = \overset{\circ}{\varepsilon}_{Hg\ |\ Hg_2^{++}} - \frac{RT}{F} \ln a_{Hg_2^{++}}^{\frac{1}{2}}$$

As the electrolyte is saturated with mercurous chloride the activity of the mercurous ions in the solution is given by the solubility product $K = a_{Hg_2^{++}} a_{Cl^-}^2$, so that:

$$a_{Hg_2^{++}} = \frac{K_s}{a_{Cl^-}^2}\ .$$

By substituting this value into the already mentioned equation the following equation will be obtained:

$$\varepsilon_{Hg\ |\ Hg_2^{++}} = \overset{\circ}{\varepsilon}_{Hg\ |\ Hg_2^{++}} - \frac{RT}{F} \ln K_s^{\frac{1}{2}} + \frac{RT}{F} \ln a_{Cl^-}.$$

The first two terms on the right hand side of the equation are constant at a given temperature and express the standard potential of the calomel electrode $\overset{\circ}{\varepsilon}_{Hg,\ Hg_2Cl_2\ |\ Cl^-}$, the activity of chloride ions equalling unity; the last formula could, therefore, be written in the form:

$$\varepsilon_{Hg,\ Hg_2Cl_2\ |\ Cl^-} = \overset{\circ}{\varepsilon}_{Hg,\ Hg_2Cl_2\ |\ Cl^-} + \frac{RT}{F} \ln a_{Cl^-}. \qquad \text{(VI-18)}$$

The same equation for the calomel electrode potential will be obtained when using the Nernst equation (VI-7) for the reaction expressed by the equation (c).

From the electrochemical point of view, the process (c) proceeding in the calomel electrode is equivalent to the reaction

$$Cl^- = \tfrac{1}{2}\, Cl_2 + e,$$

when the calomel which is partly dissociated according to equation

$$Hg_2Cl_{2(s)} = 2\, Hg_{(l)} + Cl_{2(g)}.$$

is considered as the source or consumer of chlorine

We can, therefore put the equation (VI-18) equal to the equation for the potential of the chlorine electrode (VI-16), whereby the following formula will be obtained:

$$\varepsilon^\circ_{Pt,\,Cl_2\,|\,Cl^-} - \frac{RT}{F} \ln p^{\frac{1}{2}}_{Cl_2} = \varepsilon^\circ_{Hg,\,Hg_2Cl_2\,|\,Cl^-},$$

where p_{Cl_2} is the dissociation pressure of chlorine set free from the calomel. By substituting for the standard potentials the known values at 25 °C ($\varepsilon^\circ_{Hg,\,Hg_2Cl_2\,|\,Cl^-} = -0.268$ V and $\varepsilon^\circ_{Pt,\,Cl_2\,|\,Cl^-} = -1.358$ V) into this equation, the following result will be obtained:

$$\frac{0{,}05915}{2} \log p_{Cl_2} = \varepsilon^\circ_{Pt,Cl_2\,|\,Cl^-} - \varepsilon^\circ_{Hg,Hg_2Cl_2\,|\,Cl^-} = -1.358 + 0.268 = -1.09,$$

from which the value of the dissociation pressure of chlorine is $p_{Cl_2} = 1.4 \cdot 10^{-37}$ atm.

The calomel electrode has, therefore, the same function as the chlorine electrode. It does not work at atmospheric pressure of chloride but at a very low pressure which corresponds to the equilibrium pressure of chlorine set free by the dissociation of calomel.

As already stated, the standard oxidation potential of the calomel electrode related to unity activity of the chloride ion at 25 °C is $\varepsilon^\circ_{Hg,\,Hg_2Cl\,|\,Cl^-} = -0.268$ V. Usually, however, potentials valid directly for various types of calomel electrodes are given (see Table 10).

Table. 10. Oxidation potentials of the calomel electrode at various temperatures

Electrode	ε° at t °C	ε° at 25 °C
0.1 *N*	$\varepsilon_t^\circ = -0{,}3338 + 7 \cdot 10^{-5}\,(t - 25)$ V	$\varepsilon_{25}^\circ = -0{,}3338$ V
1.0 *N*	$\varepsilon_t^\circ = -0{,}2800 + 2{,}4 \cdot 10^{-4}\,(t - 25)$ V	$\varepsilon_{25}^\circ = -0{,}2800$ V
saturated	$\varepsilon_t^\circ = -0{,}2415 + 7{,}6 \cdot 10^{-4}\,(t - 25)$ V	$\varepsilon_{25}^\circ = -0{,}2415$ V

The silver-silver chloride electrode is made of silver or silver plated platinum wire, coated with a thin layer of silver chloride, immersed into

a solution containing chloride ions. The electrochemical reaction proceeding there and expressed by a summary equation

$$Ag_{(s)} + Cl^- = AgCl_{(s)} + e,$$

can be explained in the same manner as that of the calomel electrode. Analogously it is possible to derive also the corresponding equilibrium potential, given by the equation:

$$\varepsilon_{Ag,AgCl\,|\,Cl^-} = \varepsilon^{\circ}_{Ag,AgCl\,|\,Cl^-} + \frac{RT}{F} \ln a_{Cl^-}; \quad \varepsilon^{\circ}_{Ag,AgCl\,|\,Cl^-} = -0.2223 \text{ V (at 25 °C)}.$$

Both the calomel and silver-silver chloride electrode are reversible with respect to the chloride ions; therefore, both are applied to measurements in chloride solutions.

The mercurosulphate electrode is most suitable for work with the sulphate solutions. It is prepared analogously as the calomel electrode, with one exception that the paste is composed of mercurous sulphate, ground together with mercury and an alkali metal sulphate solution of a definite concentration. In the electrode the equilibrium is attained, according to the equation

$$Hg_{(l)} + 1/2\ SO_4^{--} = 1/2\ Hg_2SO_{4(s)} + e,$$

to which the following potential belongs:

$$\varepsilon_{Hg,Hg_2SO_4\,|\,SO_4^{--}} = \varepsilon^{\circ}_{Hg,Hg_2SO_4\,|\,SO_4^{--}} + \frac{RT}{2F} \ln a_{SO_4^{--}};$$

$$\varepsilon^{\circ}_{Hg,Hg_2SO_4\,|\,SO_4^{--}} = -0.614 \text{ V (at 25 °C)}.$$

The antimony electrode is an example of electrode of the type: metal-oxide. It consists of a rod of metallic antimony, coated with a natural film of antimony trioxide and immersed into a solution with a definite hydroxyl ion concentration. Its function can be explained as follows: antimony emits at first ions into the solution

$$Sb_{(s)} = Sb^{+++} + 3e,$$

they then react with the hydroxyl ions present, giving insoluble antimony trioxide

$$Sb^{+++} + 3\ OH^- = 1/2\ Sb_2O_{3(s)} + 3/2\ H_2O_{(l)},$$

so that the resulting reaction can be written as

$$Sb_{(s)} + 3\ OH^- = 1/2\ Sb_2O_{3(s)} + 3/2\ H_2O + 3e,$$

and the corresponding equilibrium oxidation potential is:

$$\varepsilon_{Sb,Sb_2O_3\,|\,OH^-} = \varepsilon^{\circ}_{Sb,Sb_2O_3\,|\,OH^-} + \frac{RT}{F} \ln a_{OH^-}. \qquad \text{(VI-19)}$$

According to this equation the antimony electrode is reversible with respect to hydroxyl ions. The same can be said about the hydrogen ions too, because their concentration is indirectly proportionate to that of ions OH^-. Therefore, when substituting the activity of the hydrogen ion for that of the hydroxyl ion:

$$a_{OH^-} = \frac{K_v}{a_{H^+}}$$

and when replacing the two terms $\varepsilon^{\circ}_{Sb,Sb_2O_3\,|\,OH^-}$ and $\frac{RT}{F} \ln K_v$ by one constant $\varepsilon^{\circ}_{Sb,Sb_2O_3\,|\,H^+}$, the following equation will be obtained

$$\varepsilon_{Sb,Sb_2O_3\,|\,OH^-} = \varepsilon_{Sb,Sb_2O_3\,|\,H^+} = \varepsilon^{\circ}_{Sb,Sb_2O_3\,|\,OH^-} + \frac{RT}{F} \ln K_v - \frac{RT}{F} \ln a_{H^+} =$$

$$= \varepsilon^{\circ}_{Sb,Sb_2O_3\,|\,H^+} - \frac{RT}{F} \ln a_{H^+}, \qquad \text{(VI-20)}$$

which corresponds to the reaction process:

$$Sb_{(s)} + 3/2\,H_2O = 1/2\,Sb_2O_{3(s)} \mid 3\,H^+ + 3e.$$

The antimony electrode can be considered as an oxygen electrode with a very low oxygen pressure which equals the dissociation pressure of the antimony trioxide. Its standard potential, however, is not satisfactorily reproducible, because of the variable nature of the oxide covering the metallic antimony. Therefore each newly prepared electrode is calibrated by means of solutions with exactly known values of pH (regulators). When working with the antimony electrode it is necessary to keep in mind that the relation between its potential and the value $\ln a_{H^+}$, or pH is a linear one only within the range of pH = 2—8, according to Nernst's equation (VI-20). In strong acid or alkaline solutions the above relation is not valid any longer because of the higher solubility of the antimony trioxide in the measured solution.

The antimony electrode is used for pH determination when an accurate measurement is not strictly required; its advantage in comparison with other types of electrodes is a simple design and low sensitivity to various poisons.

6. Oxidation-Reduction (Redox) Electrodes

The so called oxidation-reduction potential is caused by ions of the same substance being present in the solution in two states of oxidation or valency. These combinations are known under the name of redox-systems and the potentials transmitted by such systems to the indicating, inert electrode (e. g. a platinum one) are called the redox potentials. The origin of such a potential can be explained by the tendency of ions of a certain valency state to be converted into a more stable valency state by the exchange of the

electrons with platinum or any other inert electrode. The material of such an electrode does not take part in the chemical reaction, but only acts as an intermediary in the exchange of electrons in the oxidation-reduction process taking place in the solution.

When a suitable inert electrode (usually a platinum one, sometimes also of gold) is immersed into a solution, containing e. g. the ions of stanneous and stannic salt, it can be observed that the electrode attains a certain potential the value of which depends on the ratio of the activities of ions Sn^{++} and Sn^{++++}. In a solution containing predominantly stannic ions beside a small amount of stannous ones, stannic ions show a tendency to be converted into stanneous ions by acquiring electrons from the platinum electrode:

$$Sn^{++++} + 2e = Sn^{++}.$$

Due to this removal of electrons the platinum electrode becomes positively charged with respect to the solution.

With a great surplus of stanneous ions a reverse process occurs during which the electrode will be charged negatively by the electrons set free in the process:

$$Sn^{++} = Sn^{++++} + 2e.$$

The equilibrium which will be attained between both valency states of the ion in question can be generally expressed by the equation

$$M^{z_1\uparrow} = M^{z_2\uparrow} + (z_2 - z_1)\, e,$$

where $M^{z_1\uparrow}$ and $M^{z_2\uparrow}$ are two cations of the same metal M carrying charges z_1 and z_2 respectively ($z_2 > z_1$).

Using again the formula (VI-7), for the calculation of the redox equilibrium potential the following equation first arrived at by Peters will be obtained:

$$\varepsilon_{Pt/red,\,ox} = \varepsilon^{\circ}_{Pt/red,\,ox} - \frac{RT}{(z_2 - z_1)\,F} \ln \frac{(a_2)_{ox}}{(a_1)_{red}}. \qquad \text{(VI-21)}$$

In this equation $\varepsilon^{\circ}_{Pt/red,\,ox}$ stands for the standard state electrode potential, when the activities of both ions $M^{z_1\uparrow}$ and $M^{z_2\uparrow}$ equal unity.*) Thus e. g. the electrode potential attaining equilibrium in the following process

$$Sn^{++} = Sn^{++++} + 2e,$$

is expressed by the equation:

$$\varepsilon_{Pt\,|\,Sn^{++},\,Sn^{++++}} = \varepsilon^{\circ}_{Pt\,|\,Sn^{++},\,Sn^{++++}} - \frac{RT}{2F} \ln \frac{a_{Sn^{++++}}}{a_{Sn^{++}}}.$$

*) With sufficiently diluted solutions, where practically the ionic activity may be substituted by their concentrations $\varepsilon^{\circ}_{Pt\,|\,red,ox}$ stands for the potential of a system in which the concentration of ions of both valencies is identical.

Another type of redox system is represented by electrodes immersed in a solution containing two anions of the same element in different valency states; e. g. in a system in which the solution contains both ferro-cyanide and ferri-cyanide, equilibrium between ions will be established:

$$Fe(CN)_6^{----} = Fe(CN)_6^{---} + e,$$

with a corresponding potential, given by the equation:

$$\varepsilon^{\circ}_{Pt\,|\,Fe(CN)_6^{----},\,Fe(CN)_6^{---}} = \varepsilon^{\circ}_{Pt\,|\,Fe(CN)_6^{----},\,Fe(CN)_6^{---}} - \frac{RT}{F} \ln \frac{a_{Fe(CN)_6^{---}}}{a_{Fe(CN)_6^{----}}}.$$

These formulae show that the electrode potential ε becomes more positive with the increasing ratio: concentration of the salt in lower state of oxidation to the concentration of the salt in higher state of oxidation. Theoretically, an electrode immersed in a salt solution containing only ions of the lower valency state should have the potential $+\infty$, and an electrode immersed in a solution containing only ions of the higher valency state should have the potential $-\infty$. Actually this is never the case, because no salt exists which contains ions of only one valency state. Water also as a solvent could at sufficiently high potentials react with the dissolved substance and oxidize or reduce it, to a certain extent, to a salt of another valency.

The values of standard potentials, as given in tables refer to oxidation reactions (e. g. $Fe^{++} = F^{+++} + e$); potentials defined in this way express the tendency of ions to pass over from a lower to a higher state of oxidation. The more positive the values of these standard potentials are the more stable their oxidation state, or the more energetically the reduced form tries to convert into a higher oxidation form. On the contrary, systems with considerably negative potentials are characteristic for substances with an unstable oxidation state which can easily be converted into a reduced form.

K. CHEMICAL GALVANIC CELLS

By combining two electrodes of various types galvanic cells are formed, known as chemical galvanic cells, because the electrical energy in them is generated by converting the chemical energy.

The simplest type of such a cell is a combination of two different metal electrodes which are immersed into solutions of their own salts. If the existence of the liquid junction potential at the interface of both solutions is not taken into account, or if this potential has been suppressed in a suitable manner, the *EMF* of the cell equals the total of the oxidation and reduction potentials at the electrodes. E. g. in a galvanic cell composed according the following formula

$$Zn \mid ZnSO_4/m = 0.5/ \parallel CdSO_4/m = 2.0/ \mid Cd$$

the zinc electrode is immersed into a solution of zinc sulphate having a molality

$m = 0.5$, and the cadmium electrode in a solution of cadmium sulphate having a molality $m = 2.0$, the following chemical reaction will proceed:

$$Zn_{(s)} + CdSO_4/m = 2.0/ = ZnSO_4/m = 0.5/ + Cd_{(s)}.$$

The equilibrium potentials at both electrodes of this cell are calculated from the equations:

$$Zn = Zn^{++} + 2e;\ \varepsilon_{Zn\,|\,Zn^{++}} = \varepsilon^{\circ}_{Zn\,|\,Zn^{++}} - \frac{RT}{2F} \ln a_{Zn^{++}},$$

$$Cd^{++} + 2e = Cd;\ \pi_{Cd^{++}\,|\,Cd} = \pi^{\circ}_{Cd^{++}\,|\,Cd} - \frac{RT}{2F} \ln \frac{1}{a_{Cd^{++}}}.$$

The resultant *EMF* is given by the total of both potentials, therefore:

$$E = \varepsilon_{Zn\,|\,Zn^{++}} + \pi_{Cd^{++}\,|\,Cd} = \varepsilon^{\circ}_{Zn\,|\,Zn^{++}} + \pi^{\circ}_{Cd^{++}\,|\,Cd} - \frac{RT}{2F} \ln \frac{a_{Zn^{++}}}{a_{Cd^{++}}}.$$

The oxidation potential of the zinc electrode at 25 °C is $\varepsilon^{\circ}_{Zn\,|\,Zn^{++}} = 0.762$ V and the reduction potential of the cadmium electrode is $\pi^{\circ}_{Cd^{++}\,|\,Cd} = -0.402$ V, so that

$$E^{\circ} = \varepsilon^{\circ}_{Zn\,|\,Zn^{++}} + \pi^{\circ}_{Cd^{++}\,|\,Cd} = 0.36 \text{ V}.$$

For the ion activities the products of concentrations and activity coefficients are substituted, thus $a_{Zn^{++}} = m_{Zn^{++}}\,\gamma_{Zn^{++}}$ and $a_{Cd^{++}} = m_{Cd^{++}}\,\gamma_{Cd^{++}}$. As already stated above, the mean activity coefficients of the compounds are applied for the same concentration because of the lack of knowledge of the activity coefficients of the individual ions. In a given instance Table 8 states $\gamma_{ZnSO_4} = 0.063$ and $\gamma_{CdSO_4} = 0.030$. Assuming both salts to be completely dissociated $m_{Zn^{++}} = 0.5$ and $m_{Cd^{++}} = 2$. The resultant *EMF* at 25 °C will then equal:

$$E = 0.36 - \frac{0.05915}{2} \log \frac{0.5 \cdot 0.063}{2 \cdot 0.030} = 0.3683 \text{ V}.$$

Another example of a chemical galvanic cell is the system illustrated symbolically by

$$Pt,J_{2(s)} \mid J^- (a = 1) \parallel Fe^{++}(a = 1),\ Fe^{+++}\ (a = 1) \mid Pt,$$

in which the following reaction takes place

$$J^- + Fe^{+++} = Fe^{++} + 1/2\ J_{2(s)}.$$

In the given example all reaction components possess an activity equalling unity. When calculating the *EMF* it is, therefore, only necessary to take into consideration the standard potentials of the corresponding half cells:

$$J^- = 1/2\ J_2 + e;\ \varepsilon^{\circ}_{Pt,J_2\,|\,J^-} = -0.535 \text{ V (oxidation)},$$

$$Fe^{+++} + e = Fe^{++};\ \pi^{\circ}_{Fe^{++},\,Fe^{+++}\,|\,Pt} = +0.771 \text{ V (reduction)}.$$

The resultant *EMF* is again expressed by the sum of both potentials:

$$E^{\circ} = \varepsilon^{\circ}_{Pt,J_2\,|\,J^-} + \pi^{\circ}_{Fe^{++},\,Fe^{+++}\,|\,Pt} = 0.236 \text{ V}.$$

The value of the electromotive force arrived at is positive which suggests that the reaction, proceeding in the direction of the written equation, is a spontaneous one with the negative pole of the cell at the iodine electrode.

L. CONCENTRATION GALVANIC CELLS

While chemical galvanic cells are formed by a combination of two different types of electrodes, by a combination of two identical half cells which differ only in concentration of the electromotively active substances, the so called concentration cells are obtained. In such cells the electrical energy is generated by the spontaneous transfer of the active substance from a higher to a lower potential level (e. g. by transfer from the more concentrated to the more diluted solution).

We distinguish between concentration cells without and with transference. In the first type the solutions surrounding both electrodes are not brought into direct contact, while in concentration cells with transference two solutions are in direct contact. The name "cell with transference" originates from the fact that during flow of the current a simultaneous transfer of the electrolyte takes place owing to the different ionic mobility. In the case of cells without transference the direct transfer of the electrolyte from one solution to the other is prevented; in this instance the transport of the electromotive active substance proceeds exclusively as a result of reactions taking place at the electrodes.

The *EMF* of a cell with transference is increased or decreased, as compared with the *EMF* of a cell without transference, by the value of the liquid junction potential existing at the interface of both solutions according to the sign of this and to the sign of the electrode potentials.

1. Concentration Cells without Transference

The difference in concentration which causes the potential difference within the cell is a result of either the difference in concentration of the electromotively active substance in the electrodes (with gas and amalgam concentration cells), or of the different concentration of solutions surrouding the electrodes (with electrolyte concentration cells). As will be seen later electrolyte concentration cells must be adjusted in special way in order to exclude liquid junction or diffusion potential.

a) *Gas concentration cells*

An example of a gas concentration cell is a system of two hydrogen electrodes saturated with hydrogen at different pressure ($p_1 > p_2$), both dipping into the same solution with the hydrogen ions activity a_{H^+}:

$$Pt,H_2(p_1) \mid H^+(a_{H^+}) \mid H_2(p_2), Pt.$$

Oxidation takes place at the electrode on the left where the hydrogen pressure is higher:

$$1/2\ H_2(p_1) = H^+(a_{H^+}) + e\ ,\ \varepsilon_1 = -\frac{RT}{F}\ln\frac{a_{H^+}}{p_1^{\frac{1}{2}}},^*)$$

while reduction occurs at the right electrode:

$$H^+(a_{H^+}) + e = 1/2\ H_2(p_2)\ ;\ \pi_2 = -\frac{RT}{F}\ln\frac{p_2^{\frac{1}{2}}}{a_{H^+}}.$$

By adding both equations the following result will be obtained:

$$1/2\ H_2(p_1) = 1/2\ H_2(p_2)\ ;\ E = \frac{RT}{2F}\ln\frac{p_1}{p_2}, \qquad \text{(VI-22)}$$

according to which the entire process within the cell is limited to the transfer of hydrogen from pressure p_1 down to p_2 so that gradually both pressures are equalized. Apart from this process there is no chemical reaction proceeding within the cell. It is apparent from the last mentioned equation that the ***EMF*** does not depend on the concentration of hydrogen ions in the solution.

b) *Amalgam concentration cells*

An example of this type is a cell in which two zinc amalgams, differing in concentration ($a_1 > a_2$), are dipped into a zinc salt solution with the zinc ions activity $a_{Zn^{++}}$

$$ZnHg_x(a_1)\ |\ Zn^{++}(a_{Zn^{++}})\ |\ ZnHg_x(a_2).$$

As with gas concentration cells, it can be proved also here that the electrochemical reaction during which the zinc dissolves at the left hand electrode and deposits at the right side one, can be expressed by the summary equation

$$ZnHg_x(a_1) = ZnHg_x(a_2).$$

According to this equation, the following formula is valid for the ***EMF*** of this cell:

$$E = \frac{RT}{2F}\ln\frac{a_1}{a_2} \qquad \text{(VI-23)}$$

The activity ratio can be here replaced by the corresponding concentration ratio in sufficiently diluted amalgams. It follows from this equation that the ***EMF*** of the concentration amalgam cell does not depend on the ionic activity in the solution.

c) *Electrolyte concentration cells*

In a cell formed by the combination of hydrogen and chlorine electrodes, dipped into diluted hydrochloric acid possessing the mean activity $a_{\pm}$,

*) The standard potential of the hydrogen electrode is $\varepsilon^\circ_{H_2} = 0$ at any temperature.

$$Pt,H_2(p_{H2}) \mid HCl(a_{\pm}) \mid Cl_2(p_{Cl_2}),\ Pt,$$

equilibrium is attained at the hydrogen electrode

$$1/2\ H_2 = H^+ + e;\ \varepsilon_{Pt,H_2 \mid H^+} = -\frac{RT}{F} \ln \frac{a_{H^+}}{p_{H_2}^{\frac{1}{2}}}$$

and at the chlorine electrode

$$1/2\ Cl_2 + e = Cl^-;\ \pi_{Cl^- \mid Cl_2,Pt} = \pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{a_{Cl^-}}{p_{Cl_2}^{\frac{1}{2}}}.$$

When adding both equations, it follows that the total reaction proceeding within the cell will be expressed by the equation:

$$1/2\ H_2 + 1/2\ Cl_2 = H^+ + Cl$$

and the corresponding *EMF* of the cell by the formula

$$E = \pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{a_{H^+}a_{Cl^-}}{p_{H_2}^{\frac{1}{2}}\ p_{Cl_2}^{\frac{1}{2}}} = \pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{a^2_{\pm}}{p_{H_2}^{\frac{1}{2}}\ p_{Cl_2}^{\frac{1}{2}}}.\ *)$$

Owing to the fact that the mean activity of the hydrochloric acid $a_{\pm} = m_{\pm}\gamma_{\pm}$, the last mentioned equation can be also written in the form:

$$E = \pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{m^2_{\pm}\gamma^2_{\pm}}{p_{H_2}^{\frac{1}{2}}\ p_{Cl_2}^{\frac{1}{2}}}. \qquad \text{(VI-24)}$$

When electrically connecting both cells, working under the same gas pressure but with electrolytes of different concentration $[(a_{\pm})_2 > (a_{\pm})_1]$:

$$Pt,\ H_2(p) \mid HCl(a_{\pm})_1 \mid Cl_2(p),\ Pt—Pt,\ Cl_2(p) \mid HCl(a_{\pm})_2 \mid H_2(p),\ Pt,$$

an electrolyte concentration cell without transference will be obtained and the resultant *EMF* will be expressed by the difference between the electromotive forces of the corresponding individual cells:

$$E = E' - E'' = \left[\pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{(a^2_{\pm})_1}{p_{H_2}^{\frac{1}{2}}\ p_{Cl_2}^{\frac{1}{2}}}\right] -$$

$$- \left[\pi^{\circ}_{Cl^- \mid Cl_2,Pt} - \frac{RT}{F} \ln \frac{(a^2_{\pm})_2}{p_{H_2}^{\frac{1}{2}}\ p_{Cl_2}^{\frac{1}{2}}}\right] =$$

$$= \frac{2RT}{F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1} = \frac{2RT}{F} \ln \frac{(m_{\pm})_2(\gamma_{\pm})_2}{(m_{\pm})_1(\gamma_{\pm})_1}. \qquad \text{(VI-25)}$$

*) $a_{H^+}\ a_{Cl^-} = a^2_{\pm}$ (see the formula V-34).

When $(a_{\pm})_2 > (a_{\pm})_1$, the resultant *EMF* has a positive sign, so that the hydrogen electrode written on the left represents the negative pole of the entire system. Under this condition the *EMF* of the first (left) cell is greater and so overcomes the lesser opposite electromotive force of the second cell in which, therefore, a reversed process occurs, i. e. the electrolysis.

The processes occurring in the individual cells can be expressed by the following equations:

$$1/2\ H_2 + 1/2\ Cl_2 = HCl(a_{\pm})_1 \qquad \text{(left hand cell)},$$

$$HCl(a_{\pm})_2 = 1/2\ H_2 + 1/2\ Cl_2 \qquad \text{(right hand cell)},$$

$$HCl(a_{\pm})_2 = HCl(a_{\pm})_1 \qquad \text{(the overall reaction of the entire system)}.$$

It is immediately evident from these equations why the hydrochloric acid concentration in the first cell increases, and in the second decreases. The process proceeds until the current becomes zero, i. e. until the activity and, therefore, the concentration of the hydrochloric acid in both cells will finally equal $[(a_{\pm})_1 = (a_{\pm})_2]$. The electromotive force of the described double cell has its origin in a reversible transference of hydrochloric acid from higher to lower concentration.

Should the order of the electrodes in both cells change so that the chlorine electrodes become the outer ones, the resultant *EMF* would be negative because the right hand electrode becomes the negative pole of the system.

The general formula for calculating the *EMF* of an electrolyte concentration cell without transference is:

$$E = \pm \frac{\nu}{\nu_{\pm}} \frac{RT}{z_{\pm}F} \ln \frac{(a_{\pm})_2}{(a_{\pm})_1}. \qquad \text{(VI-26)}$$

In this formula ν_+, or ν_- indicates the number of positive or negative ions, produced in the dissociation of one molecule of the electrolyte, taking part in the reversible process at the external electrodes; ν expresses the total number of ions ($\nu = \nu_+ + \nu_-$) and z_+ or z_- the number of charges of the ion with respect to which the external electrodes are reversible. Should this ion be positive the above mentioned formula will have a positive sign; otherwise it will be negative. The mean ionic activity of the electrolyte at the left side of the system is marked $(a_{\pm})_1$, while $(a_{\pm})_2$ signifies the same value at the right side.

2. Concentration cells with transference

In a concentration cell with transference two solutions of different concentration are brought into direct contact, either in a suitably designed junction, or by means of a porous diaphragm. At the interface of both solutions an electric double layer is formed the potential difference across which must be included into the total electromotive force of the cell. Before deriving, however, the relations for determining the *EMF* of such cells, the origin and magnitude

of the liquid junction potential (the seat of which is the interface of these two electrolytes) will be explained.

a) *The liquid junction (diffusion) potential*

The liquid junction potential will occur when diffusion of ions from the stronger to the weaker solution takes place. The rate of diffusion of every individual ion is then almost proportional to its velocity in the electric field. When the diffusion rate of the cation is higher than that of the anion more cations enter the more diluted solution which becomes positively charged. In a more concentrated solution so remains an excess of the less rapidly diffusing anion, causing that the solution becomes negatively charged. Due to the fact that the opposite charges are separated in both liquid layers, electrostatic forces of attraction will be asserted which prevent further independent diffusion of both kinds of ions. Through this influence the more mobile ions are retarded by the slower ones, and vice versa, the less mobile ions are accelerated by the more mobile ones. Finally a stationary equilibrium will be attained at which both ions have the same velocity. The tendency of ions with greater mobility to penetrate more quickly into the more diluted solution gives rise to a layer of identically charged ions followed close behind it by a layer of less mobile ions of an opposite charge. Thus, at the interface of two differently concentrated solutions an electric double layer will be formed with the diffusion, or liquid junction potential across it.

Due to the liquid junction potential having an indefinite value often varying even with time, its existence during electrochemical measurements is rather unconvenient. Fortunately this potential is not very large (reaching a maximum of approximately 50 mV), so it can be disregarded in technical calculations. For exact measurement it is advisable to eliminate it by a suitable arrangement of the cell. Where this course is not possible the liquid junction potential is eliminated to a large extent by means of the so called salt bridge; in some simple cases its value can be also approximately calculated.

A salt bridge is a liquid junction filled with a normal solution, or better, with a saturated solution of potassium chloride; where the formation of a precipitate would be the result of the contact between the solution and the electrolyte containing e. g. ions Ag^+, Tl^+, Hg_2^{++}, a saturated solution of ammonium nitrate is applied. This junction is interposed between the electrolytes surrounding both electrodes and at the same time is an intermediary of their electric connection. In this way, instead of one interface between the electrolytes, two are formed, as is evident, e. g. from the schematic representation of this system:

$$\overset{-}{H_2}(1\ \text{atm}) \mid HCl(0.01\ N) \underset{I}{\overset{- +}{\mid}} KCl(\text{sat.}) \underset{II}{\overset{+ -}{\mid}} HCl\ (0.1N) \mid \overset{+}{H_2}\ (1\ \text{atm}).$$

Both interfaces are indicated simply by a double vertical line

$$H_2(1\ \text{atm}) \mid HCl(0.01\ N) \parallel HCl(0.1\ N) \mid H_2(1\ \text{atm}),$$

which indicates the elimination of the liquid junction potential in such a cell.

As already stated the liquid junction potential results from the different mobility of ions. Consequently no diffusion potential can result at the junction of the electrolyte solution the ions of which migrate with the same velocity. It is just this principle on which the salt bridge, filled by solutions of those salts the ions of which have approximately the same mobilities, is based (the equivalent conductivities of ions K^+ and Cl^- at infinite dilution at 25 °C are 73.5 and 76.3 respectively and the conductivities of ions NH_4^+ and NO_3^- are 73.4 and 71.4 respectively). Because ions of these salts have approximately the same tendency to transfer their charge to the more diluted solution during diffusion, practically no electric double layer is formed and thus no diffusion potential either. The effect of the salt bridge on the suppression of the diffusion potential will be better, the more concentrated the salt solution is with which it is filled because the ions of the salt are considerably in excess at the solution boundary and carry, therefore, almost exclusively the electric current across this boundary.

As already mentioned, the magnitude of the diffusion potential can be approximately calculated only in some special instances; in general, this problem has not yet been solved by electrochemistry. One of the above mentioned special cases is the combination of two different uni-univalent electrolytes, having a common ion and an identical concentration, such as.

$$\begin{aligned} &HCl(c) \mid KCl(c), \\ &KCl(c) \mid NaCl(c), \\ &NaCl(c) \mid NaNO_3(c). \end{aligned}$$

The liquid junction potential ε_K is in this case calculated according to the formula

$$\varepsilon_K = \frac{RT}{F} \ln \frac{\Lambda_{HCl}}{\Lambda_{KCl}}. \qquad \text{(VI-27)}$$

in which Λ_{HCl} and Λ_{KCl} indicate the equivalent conductivities of both solutions.

A second instance, where the value of the diffusion potential can be under certain conditions ascertained by calculation, is the system in which two solutions of the same electrolyte, but of different concentration, are in contact. The method of such calculation will be illustrated by an example of a concentration cell with transference composed of two hydrogen electrodes, dipped into hydrochloric acid solutions with different concentrations which are in direct contact:

$$Pt,\ H_2(p) \mid HCl(a_+)_1 \mid HCl(a_+)_2 \mid H_2(p),\ Pt.$$

When $(a_\pm)_2 > (a_\pm)_1$, the electrons pass during the cell operation through the external conductor from the left to the right electrode and within the cell the negatively charged chloride ions migrate from the right to the left electrode, while the positively charged hydrogen ions migrate in the opposite direction:

$$\mathrm{Pt, H_2 \mid HCl}(a_{\pm})_1 \quad \vdots \quad \mathrm{HCl}(a_{\pm})_2 \mid \mathrm{H_2, Pt}$$

$$\xrightarrow{t_+}\mathrm{H^+}$$

$$1/2\ \mathrm{H_2} \rightarrow \mathrm{H^+} \qquad\qquad \mathrm{H^+} \rightarrow 1/2\ \mathrm{H_2}$$

$$\mathrm{Cl^-}\xleftarrow{t_-}$$

Since in this process the ions enter a solution of concentration which differs from the one in which they started, migration is accompanied by a change in free energy, measured by the electric potential ε_K, arising at the boundary of both liquids ($\Delta G = -\varepsilon_K F$). When a charge of one faraday is flowing through the cell, t_+ gram-ions of the H^+ migrate from the solution, with an activity $(a_+)_1$ to the solution, with a hydrogen ion activity $(a_\pm)_2$ and the t_- gram-ions of the Cl^- in the opposite direction. The total change in free energy is, therefore, expressed by the equation

$$\Delta G = -\varepsilon_K F = t_+ RT \ln \frac{(a_+)_2}{(a_+)_1} + t_- RT \ln \frac{(a_-)_1}{(a_-)_2},$$

assuming that the transference numbers of ions are independent on the concentration of the solution.

Since $t_+ + t_- = 1$ and the mean activity $a_\pm^2 = a_+ \cdot a_-$, it further follows:

$$e_K = 2t_- \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} - \frac{RT}{F} \ln \frac{(a_+)_2}{(a_+)_1} = -2t_+ \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} + \\ + \frac{RT}{F} \ln \frac{(a_-)_2}{(a_-)_1}. \qquad \text{(VI-28)}$$

For the purpose of exact calculation of the liquid junction potential according to the last mentioned equation the activity coefficient of the hydrogen or chloride ions would have to be known. As their value is unknown it is assumed that their ratio is equal to the ratio of the mean activity coefficients of hydrochloric acid, or in other words $(a_+)_2/(a_+)_1 = (a_\pm)_2/(a_\pm)_1$. Then the equation (VI-28) will be written in this form:

$$\varepsilon_K = (2t_- - 1) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1} = (t_- - t_+) \frac{RT}{F} \ln \frac{(a_\pm)_2}{(a_\pm)_1}. \qquad \text{(VI-29)}$$

The formula (VI-29) is valid for any uni-univalent electrolyte. It is evident from this formula that the sign of the liquid junction potential and also the orientation of the diffusion double layer, in respect to the double layer at the electrodes, depends on the relative magnitude of the anion and cation transference numbers. Should the anion transference number exceed that of cation

(e. g. with $AgNO_3$), the positive half of the electric double layer would be on the side of the more concentrated solution. An opposite situation arises in the case of HCl.

b) *The EMF of concentration cells with transference*

It has already been mentioned that the electromotive force of concentration cells with transference is the sum of the both electrode potentials and the liquid junction potential which arises, when two solutions of the same substance but of different concentrations are brought into contact; the value of the mentioned potential is finally given by the equations (VI-28) and (VI-29).

Applying again the already mentioned example of the concentration cell composed of two identical hydrogen electrodes immersed into hydrochloric acid solutions of different concentration $(a_{\pm})_2 > (a_{\pm})_1$, it is necessary to bear in mind the following individual potentials, when calculating the *EMF*:

$$\mathrm{Pt,\ H_2}(p) \mid (\mathrm{HCl}(a_{\pm})_1;\ \varepsilon_{\mathrm{Pt,\ H_2\mid H^+}} = -\frac{RT}{F}\ln\frac{(a_+)_1}{\sqrt[2]{p_{\mathrm{H_2}}}};$$

$$\mathrm{HCl}(a_{\pm})_2 \mid \mathrm{H_2}(p),\ \mathrm{Pt};\ \pi_{\mathrm{H^+\mid H_2,\ Pt}} = -\frac{RT}{F}\ln\frac{\sqrt[2]{p_{\mathrm{H_2}}}}{(a_+)_2};$$

$$\mathrm{HCl}(a_{\pm})_1 \mid \mathrm{HCl}(a_{\pm})_{12};\ \varepsilon_K = 2t_-\frac{RT}{F}\ln\frac{(a_{\pm})_2}{(a_{\pm})_1} - \frac{RT}{F}\ln\frac{(a_+)_2}{(a_+)_1};\text{*)}$$

$$E = \varepsilon_{\mathrm{Pt,\ H_2\mid H^+}} + \pi_{\mathrm{H^+\mid H_2,\ Pt}} + \varepsilon_K = 2t_-\frac{RT}{F}\ln\frac{(a_{\pm})_2}{(a_{\pm})_1} =$$

$$= 2t_-\frac{RT}{F}\ln\frac{(m_{\pm})_2(\gamma_{\pm})_2}{(m_{\pm})_1(\gamma_{+})_1}. \qquad \text{(VI-30)}$$

As can be seen from the result, the formula for the calculation of the *EMF* of a cell, which is reversible with respect to cations (in this case to hydrogen ions), contains the transference number of anion (chloride ion).

When dipping two identical chlorine electrodes into two hydrochloric acid solutions of different concentrations $[(a_{\pm})_2 > (a_{\pm})_1]$ instead of the hydrogen electrodes, a concentration cell with transference will be obtained, reversible with respect to the anions:

$$\mathrm{Pt,\ Cl_2}(p) \mid \mathrm{HCl}\ (a_{\pm})_1 \mid \mathrm{HCl}\ (a_{\pm})_2 \mid \mathrm{Cl_2}\ (p),\ \mathrm{Pt}.$$

The *EMF* is again equal to the total of the potentials at both electrodes and the liquid junction potential:

*) see equation (VI-28).

$$\mathrm{Pt,\ Cl_2}(p)\,|\,\mathrm{HCl}(a_\pm)_1;\ \varepsilon_{\mathrm{Pt,\,Cl_2\,|\,Cl^-}} = \overset{\circ}{\varepsilon}_{\mathrm{Pt,\,Cl_2\,|\,Cl^-}} - \frac{RT}{F}\ln\frac{p_{\mathrm{Cl_2}}^{\frac{1}{2}}}{(a_-)_1};$$

$$\mathrm{HCl}(a_\pm)_2\,|\,\mathrm{Cl_2}(p),\mathrm{Pt};\ \pi_{\mathrm{Cl^-\,|\,Cl_2,Pt}} = \overset{\circ}{\pi}_{\mathrm{Cl^-\,|\,Cl_2,Pt}} - \frac{RT}{F}\ln\frac{(a_-)_2}{p_{\mathrm{Cl_2}}^{\frac{1}{2}}};$$

$$\mathrm{HCl}(a_\pm)_1\,|\,\mathrm{HCl}(a_\pm)_2;\ \varepsilon_K = -2t_+\frac{RT}{F}\ln\frac{(a_\pm)_2}{(a_\pm)_1} + \frac{RT}{F}\ln\frac{(a_-)_2}{(a_-)_1};^{**})$$

$$E = \varepsilon_{\mathrm{Pt,\,Cl_2\,|\,Cl^-}} + \pi_{\mathrm{Cl^-\,|\,Cl_2,Pt}} + \varepsilon_K = -2\,t_+\frac{RT}{F}\ln\frac{(a_\pm)_2}{(a_\pm)_1} =$$

$$= -2t_+\frac{RT}{F}\ln\frac{(m_\pm)_2(\gamma_\pm)_2}{(m_\pm)_1(\gamma_\pm)_1} \qquad \text{(VI-31)}$$

The resultant *EMF* has a negative sign which proves that the electrode written on the left side receives a positive charge because the gaseous chlorine passes into an ionic state due to the lower osmotic pressure of the chlorine ions in the solution $[(a_\pm)_1 < (a_\pm)_2]$. The electric current, therefore, flows through the cell in an opposite direction to that of a reversible cell with respect to cations.

The influence of the relative values of the transference numbers, affecting the resultant value of the *EMF* of the concentration cell without transference, is clearly to be seen from the equation (VI-29); should $t_- > t_+$ then ε_K is positive and in a concentration cell reversible with respect to cations the liquid junction potential is added to the sum of the electrode potentials; should, however, $t_- < t_+$, then the liquid junction potential will lower the resultant *EMF*. In a concentration cell reversible with respect to anions (e. g. in a cell with chlorine electrodes) the *EMF* is decreased when $t_- > t_+$, and increased when $t_- < t_+$.

The formulae (VI-30) and (VI-31) for calculating *EMF* of concentration cells with transference are valid for the uni-univalent electrolyte. For any arbitrary electrolyte both formulae are written in a general form,

$$E = \pm t_\mp\frac{\nu}{\nu_\pm}\frac{RT}{z_\pm F}\ln\frac{(a_\pm)_2}{(a_\pm)_1}, \qquad \text{(VI-32)}$$

where t_- and t_+ are the anion and cation transference numbers, and other symbols have the same meaning, as in the formula (VI-26).

According to all the equations derived the *EMF* of the concentration cell does not depend on the magnitude of the electrode potentials, but solely on the logarithm of the ratio of activities of electromotively active components in both

**) see equation (VI-28).

solutions, since no chemical reaction is proceeding in the cell, but a physical process consisting of transporting the substance from the more to the less concentrated solution. The factor by which the logarithm of the activity ratio has to be multiplied depends on the number of gram-ions transferred within the cell at a flow of one faraday.

Cells combined in a suitable manner are applied in technical practice as the source of direct current. In theoretical electrochemistry the measuring of the electromotive forces of suitably combined systems of electrodes is of great importance for the purpose of determining various electrochemical constants (e. g. activity coefficients, dissociation constants of the weak electrolytes, ionic transference numbers, solubility products of sparingly soluble salts etc.). From the magnitude of the electromotive forces and their thermal coefficients the change in free energy can also be determined, as well as the heat of reaction and the change in entropy of the reaction proceeding in the galvanic cell.

VII. ELECTROLYSIS AND POLARIZATION

In the last chapter it has been explained, how chemical energy can be changed into electric one. It has been pointed out that only such reactions can be applied to electric current generation which are accompanied by a certain decrease of free energy ΔG and are divisible within the galvanic cell into two partial processes proceeding at two spacially distant electrodes. Contrary to these reactions there are processes where the free energy of the products is greater than that of the starting substances. When the substances are electrochemically active then it is possible to carry out these reactions elektrolytically and supply the energy to the systems, in order to raise the free energy of the products above that of the reactants. Electrolytical processes are of great industrial importance because they often permit to obtain the required reaction products in a simpler and more economical way than by purely chemical reactions. Sometimes electrolysis is the only method of producing a certain substance.

A. OHM'S LAW ADAPTED FOR ELECTROLYSIS

A reversibly operating electrochemical system can act either as a galvanic cell or as an electrolyzer. Let us imagine, e. g. a system composed of a hydrogen and a chlorine electrode wich are immersed into hydrochloric acid with a mean activity equal to unity. The platinum electrodes are surrounded by a hydrogen or chlorine atmosphere at a pressure of 1 atm. The system is, therefore, in its standard state, having at 25 °C an *EMF* of 1.358 V. The electrodes of the cell are connected to the corresponding poles of the external current source in a potentiometric circuit. As long as the voltage supplied from the external source is within the range of zero to 1.358 V, the system operates as a galvanic cell generating electric energy while both gases at the electrodes are transferred into their respective ionic state:

$$\tfrac{1}{2}\,H_2 = H^+ + e,$$
$$\tfrac{1}{2}\,Cl_2 + e = Cl^-.$$

If the external compensating voltage equals exactly the *EMF* of the cell, all current will cease to flow through the circuit and the cell will stop functioning. Should, however, the external voltage exceed 1.358 V, the initial current flow direction will be reversed and the electrons from the external current source enter the hydrogen electrode and flow through the cell (in ionic form), and emerge again at the chlorine electrode from where they return to the current source. Since external electrons are fed to the hydrogen electrode, generally called the cathode, and from the chlorine electrode, i. e. from the anode, electrons are taken away, the system compensates the equilibrium disturbance

by consuming the surplus electrons at the hydrogen electrode in the process:

$$H^+ + e = \tfrac{1}{2} H_2.$$

Electrons drawn away from the chlorine electrode are replaced by new ones, produced in the reaction:

$$Cl^- = \tfrac{1}{2} Cl_2 + e.$$

These processes change the initial spontaneous reaction so, that at the hydrogen electrode where formerly oxidation occurred reduction takes place, while at the chloride electrode the reduction process is replaced by oxidation. The total reaction in the electrolyzer which proceeds in an opposite direction to that in the galvanic cell can be expressed by the equation:

$$H^+ + Cl^- = \tfrac{1}{2} H_2 + \tfrac{1}{2} Cl_2.$$

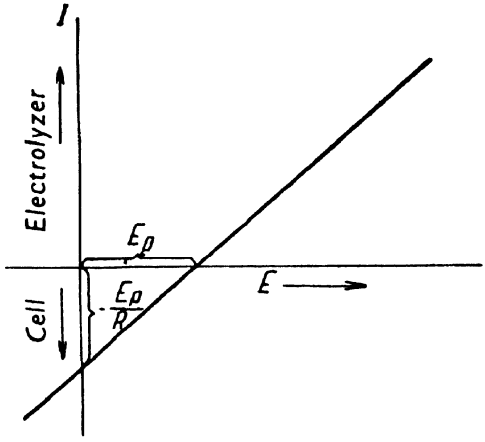


Fig. 15. The relation of current I flowing through an electrolyzer to the voltage of the external source of current in a system with constant polarization voltage E_p.

From this example it can be seen that electrolysis will start only when the external voltage will exceed the value E_p of the electromotive force of the galvanic cell which acts in a direction opposite to the electrolyzing current. The value E_p can also be considered as the expression of the effort of the system to maintain the initial state (in this case the tendency of the hydrogen and chloride ions to stay in the ionic state). Therefore, for the current flowing through the electrolyzer and also for the production capacity of the system, the entire voltage of the external current source E is not decisive, but the difference $E - E_p$. If the resistance of the electrolyte and the external circuit is R, Ohm's law can be applied to the electrolyzer in the form:

$$E - E_p = IR. \qquad \text{(VII-1)}$$

Electrochemical energy proportional to the potential difference $E - E_p$ which is consumed according to this formula to overcome the resistance R of both the electrolyte and the external circuit, is finally converted into heat which increases the temperature of the electrolyte and current conductors.

If electrolysis is carried out under reversible conditions at a constant temperature and electrolyte composition, the E_p remains constant, too. Under this assumption the graphical representation of the equation (VII-1) is illustrated

in Fig. 15 in which the current flowing through the system is plotted against voltage E of the external current source. It follows from the equation (VII-1), that as long as the external voltage is not applied at all, the current flowing through the system equals the ratio of the EMS and the resistance R. This current is shown in the diagram by the ordinate for $E = 0$. As long as the external current voltage is smaller than E_p the system will act as a galvanic cell producing the current the magnitude of which is represented on the negative side of the axis of ordinates. In the point of intersection of the current curve and the axis of abscissae no current is flowing through the system, the electromotive force of which being just compensated by the voltage of the external source of current ($E = E_p$). When finally $E > E_p$ the cell acts as an electrolyzer through which flows the electrolyzing current the magnitude of which is represented on the positive side of the axis of abscissae. The slope of the current line is given by the value of the resistance R.

Let us now consider the same system in which the platinum electrodes are not surrounded by hydrogen and chlorine atmosphere, before operation is started, and do not show any EMF of its own. In this case no current will flow after closing the electric circuit. In the face of this it appears that no back electromotive force E_p will weaken the electrolyzing voltage and so the entire value of E will be used for the formation of the electric field between the electrodes. But it is not so. Although the current begins to flow across the electrolyzer yet at very low terminal voltage, is the duration of the flow very limited. This can be seen on a galvanometer which is connected in series, by the quick return of its pointer to zero position. This phenomenon is due to the small amount of current flowing across the electrolyzer, which causes a discharge of a negligible quantity of hydrogen ions at the cathode and chloride ions at the anode. Both gases which are liberated at a very low partial pressure are dissolved in the platinum electrodes, but they do not escape to surroundings, where is a much higher pressure. Through the dissolution of gases in the platinum the originally electromotively inactive electrodes will become active; the electrode with dissolved hydrogen will become capable of emitting hydrogen ions into the solution and the other electrode will acquire the nature of a chlorine electrode with a tendency to form chloride ions. This change in the nature of the electrodes gives rise to the back electromotive force. As long as $E < E_p$, the back EMF has a magnitude, which suffices to compensate the external voltage, against which it is directed. Therefore, no current can flow between the electrodes.

With a rising voltage across the electrolyzer the back electromotive force will rise in proportion, because gases will be evolved and dissolved at a higher pressure in the platinum electrodes. When this pressure rises to 1 atm., the gases will be able to overcome the ambient atmospheric pressure and begin to escape freely into the atmosphere in the form of bubbles. Should this process proceed under reversible conditions and should the concentration of hydrochloric acid during electrolysis remain constant, the back electromotive force

attains at that moment the maximum value E_p. There will be no rise in E_p with a further rise in the terminal voltage, because the conditions in which the gases are evolved at the electrodes do not change any more.

Due to the flow of current the original system reached the same active state as in the first example, when it consisted from the beginning of hydrogen and chlorine electrodes. Therefore, the attained value E_p must be theoretically of the same magnitude, as the *EMF* of a galvanic cell, operating under the same conditions (in the given example $E_p = 1.358$ V). In the graphical representation (see Fig. 16) the relation $E - I$ is expressed by a straight line commencing at the origin of coordinates O and running along the axis of abscissae to the point E_p; this point represents the voltage value at which the gases are attaining the pressure of 1 atm. and at which the current begins to flow continuously through the electrolyzer. Here the straight line breaks upwards and proceeds steeply in accordance with the rapidly rising current (E_pD).

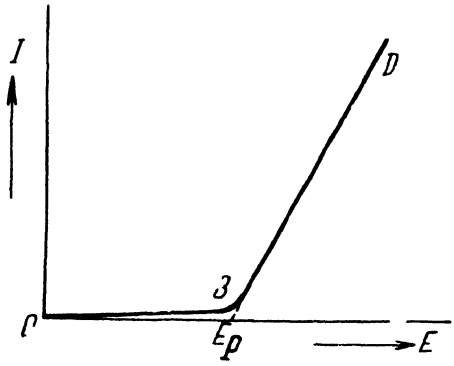


Fig. 16. The curve of decomposition voltage.

It has been already said that the back electromotive force makes up for the electrolyzing voltage, as long as $E < E_p$. This is, however, not exactly expressed as actually some current flows through the system even before the decomposition voltage E_p is reached (see Fig. 16, line OB). This small current, called residual current, is caused by the fact that the products of electrolysis (chlorine and hydrogen) do not permanently remain in the electrodes, as theoretically assumed, but a small quantity is lost by dissolution in the surrounding electrolyte and by diffusion into the bulk of electrolyte. These losses are compensated by the residual current.

The phenomenon of formation of the *EMF* during the electrolysis is encountered not only with gas electrodes, but also with metal electrodes, e. g. the originally electromotively inert platinum electrode which acts as a cathode and is immersed in a zinc sulphate solution, becomes coated with a layer of metallic zinc and acquires the potential corresponding to the Zn/Zn^{++} system.

In the last two examples the back electromotive force which arises in the system during the electrolysis, acts against the electrolyzing voltage and compensates it in a certain range. Such a process, in the course of which the flow of current through the electrolyzer causes a change in the electrode potentials is generally called **polarization**; the electromotive force which arises is called **polarization voltage** and the external current source voltage the **polarizing voltage**.

In addition to the described type of polarization there is a further type of polarization, which is due to the slowness of one or several processes taking place at the electrodes during discharge and ion formation. Consequently, the electrodes are disturbed in their equilibrium conditions and their potentials exceed their values corresponding to the state when a very weak current or none at all flows through the electrodes.*) Concentration polarization, overvoltage and passivity are these types of polarization and will be dealt with in detail later on.

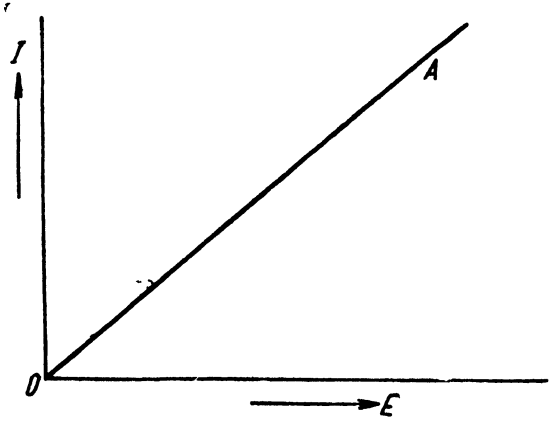


Fig. 17. The voltage E of the external source of current plotted against the current I passing through an electrolyzer consisting of two equal unpolarizable electrodes.

The slowness of the electrode processes when a stronger current flows through the electrolyzer results in an increase of the back electromotive force E_p, above its theoretical value (i. e. above the EMF of the corresponding galvanic cell). In such an instance Ohm's law (see formula VII-1) will still be valid but the value E_p will no longer be constant but will increase in proportion to the current density and will also depend on the duration of the electrolysis.

Ohm's law written in the form $E = IR$ is valid only in a system which consists of two equal unpolarizable electrodes immersed in a common electrolyte the potential of which will not change during the flow of an actual current through the electrolyzer. Under this condition the electrode potentials are mutually cancelled ($E_p = 0$), so that the equation (VII-1) will be simplified to the form $E = IR$. The relation between the electrolyzer voltage and the current flowing through it is represented, therefore, in the diagram by a straight

*) Some electrodes attain much higher potentials than the reversible ones at the flow of very small current, and behave in an irreversible manner at all conditions (e. g. the oxygen electrode).

line OA, starting at the origin of coordinates and the slope of which is determined by the magnitude of the electrolyte resistance (see Fig. 17).

An unpolarizable system can be formed by two identical electrodes with which neither concentration polarization, overvoltage, nor passivity will appear. As a matter of fact a combination approaching most closely to this ideal system consists of two electrodes of the second class (e. g. calomel electrodes) in which concentration polarization is prevented by maintaining the concentration of the electromotively active ion in the solution round the electrodes constant when the current flows through. If we ignore concentration polarization which is generally not very large, even a combination of two electrodes of the first class with a common electrolyte can be considered as an unpolarizable system. Such is the case in industrial practice of electrometallurgical refining processes. For example in a copper refining process the crude impure metal which forms the anode enters the copper sulphate solution acidified by sulphuric acid, and is deposited on the cathode in its pure form. In such an electrolyzer the potentials at both electrodes differ practically in the sign only. That means that the work necessary to dissolve copper equals approximately the work obtained at copper deposition from its ionic state. Therefore, the current overcomes the resistance of the electrolyte only and does not perform any other work.

B. DECOMPOSITION VOLTAGE

The smallest value of the voltage of external current source at which permanent current starts to flow and uninterrupted electrolysis begins is called the decomposition voltage of the respective electrolyte E_R. When substituting this condition ($I = 0$) in the equation (VII-1), the following formula will be obtained:

$$E = E_P = E_R \text{ (for } I = 0) \qquad \text{(VII-2)}$$

From this it follows that E_R has the same magnitude as the polarization voltage of the system at the beginning of the continuous electrolysis.

Although according to modern views the decomposition potential is not thought to possess any exact theoretical significance it is still applied when the yields of energy are calculated (see equation II-11). When the system is working under reversible conditions, the value of the decomposition voltage can be deduced theoretically. If this condition is not fulfilled, the unknown decomposition voltage can be determined experimentally from the current-voltage curves.

1. Theoretical decomposition voltage

The first mathematical method is based on the equivalence of minimum energy ($-W'$) which has to be supplied to the electrolyzer in the form of electric current and the change in free energy $\Delta G'$ accompanying the considered

electrolytic process. The relation between both values is then identical to that valid for galvanic cells. The minimum work to be done (— W') is theoretically equal to the maximum work obtained if the products of electrolysis are allowed to react in the opposite direction and the initial substances are again obtained:

$$(-W') = -nFE'_{\min} = \Delta G', \text{ or } E'_{\min} = -\frac{\Delta G'}{23\,066\,n}. \qquad \text{(VII-3)}$$

Since all electrolytic processes are characterized by the positive value of $\Delta G'$, the voltage $E'_{\min}$, will always have the negative sign which is an indication that the electrolytic process is not a spontaneous one but requires a supply of energy from an external source.

As far as the equation (VII-2) is concerned the potential difference $E'_{\min}$ represents the negative value of the theoretical decomposition voltage $(E_R)_t$, necessary for the beginning of the electrolysis in a reversibly operating system. When substituting the relation $E'_{\min} = -(E_R)_t$ into the equation (VII-3), we obtain

$$(E_R)_t = \frac{\Delta G'}{23\,066\,n}, \qquad \text{(VII-4)}$$

from which the theoretical decomposition voltage in a certain electrolysis can be arrived at if we know the reaction taking place and the respective value of the free energy change.

Should, e. g. the decomposition of hydrogen iodide solution ($a_{HJ} = 1$), proceeding according to the equation

$$HJ = \tfrac{1}{2}\,H_2 + \tfrac{1}{2}\,J_2,$$

be accompanied (at 25 °C and 1 atm. pressure) by the increase of free energy $\Delta G' = 12.330$ cal, the theoretical decomposition voltage of such an electrolyte will be, according to formula (VII-4):

$$(E_R)_t = \frac{12\,330}{23\,066} = 0.535 \text{ V}.$$

The same potential would be shown by a galvanic cell combined of standard iodine and hydrogen electrodes immersed in a hydrogen iodide solution with activity $a = 1$. In this galvanic cell the above mentioned reaction would proceed spontaneously in the opposite direction. Should this spontaneous process be inhibited during the course of electrolysis the external voltage must be at least of a magnitude, capable of overcoming the electromotive force of the galvanic cell. From this is evident the significance of the decomposition voltage, being the lowest voltage value across the electrolyzer terminals above which the undisturbed electrolysis starts to proceed.

Theoretical decomposition voltage can also be calculated from the reversible electrode potentials. Because the potential difference $E'_{\min}$ equals, according

to equation (VI-6a), the sum total of the oxidation potential at the anode ε_A and the reduction potential at the cathode π_K, the following equation is valid with simultaneous regard to the relation $E'_{min} = -(E_R)_t$:

$$E'_{min} = -(E_R)_t = \varepsilon_A + \pi_K = \varepsilon_A - \varepsilon_K = -\pi_A + \pi_K$$

or

$$(E_R)_t = \pi_A - \pi_K. \qquad \text{(VII-5)}$$

As an example we quote the electrolysis of zinc chloride solution with molal concentration $m = 0.5$, at a pressure of 1 atm. and temperature 25 °C. The mean activity coefficient of zinc chloride at this concentration $\gamma_{\pm m} = 0.51$. At the zinc ions concentration $m_{Zn^{++}} = 0.5$ and at that of chloride ions $m_{Cl^-} = 1.0$, the respective ion activity equals $a_{Zn^{++}} = 0.5 \cdot 0.51 = 0.255$ and $a_{Cl^-} = 0.51$. The theoretical decomposition voltage of the zinc chloride in this solution will be according to formula (VII-5):

$$\text{anode: } 2\,Cl^- = Cl_2 + 2e;\ \varepsilon_{Pt,Cl_2|Cl^-} = \varepsilon^\circ_{Pt,Cl_2|Cl^-} - \frac{RT}{2F}\ln\frac{p_{Cl_2}}{a^2_{Cl^-}} =$$

$$= -1.358 - \frac{0.05915}{2}\log\frac{1}{0.51^2} = -1.375,$$

$$\text{cathode: } Zn^{++} + 2e = Zn;\ \pi_{Zn^{++}|Zn} = \pi^\circ_{Zn^{++}|Zn} - \frac{RT}{2F}\ln\frac{1}{a_{Zn^{++}}} =$$

$$= -0.762 - \frac{0.05915}{2}\log\frac{1}{0.255} = -0.780,$$

$$E'_{min} = \varepsilon_{Pt,Cl_2|Cl^-} + \pi_{Zn^{++}|Zn} = -1.375 - 0.780 = -2.155\,V;\ (E_R)_t = 2.155\,V.$$

To determine the theoretical decomposition voltage of hydrochloric acid in solution with molal concentration $m = 1$ at a pressure of 1 atm. and temperature 25 °C with $\gamma_{\pm m} = 0.811$, the same procedure will be used:

$$\text{anode: } 2Cl^- = Cl_2 + 2e;\ \varepsilon_{Pt,Cl_2|Cl^-} = \varepsilon^\circ_{Pt,Cl_2|Cl^-} - \frac{RT}{2F}\ln\frac{p_{Cl_2}}{a^2_{Cl^-}} =$$

$$= -1.358 - \frac{0.05915}{2}\log\frac{1}{0.811^2} = -1.363,$$

$$\text{cathode: } 2\,H^+ + 2e = H_2;\ \pi_{H^+|H_2,Pt} = -\frac{RT}{2F}\ln\frac{p_{H_2}}{a^2_{H^+}} =$$

$$= -\frac{0.05915}{2}\log\frac{1}{0.811^2} = -0.005.$$

$$E'_{min} = \varepsilon_{Pt,Cl_2|Cl^-} + \pi_{H^+|H_2,Pt} = -1.363 - 0.005 = -1.368\,V;\ (E_R)_t = 1.368\,V.$$

When calculating the theoretical decomposition of those salts, which liberate oxygen at the anode during electrolysis, the standard potential of the oxygen electrode has to be applied. In the electrolysis of, e. g. cadmium sulphate, having a molal concentration $m = 1$ ($\gamma_{\pm m} = 0.042$), from the neutral solution ($a_{H^+} = a_{OH^-} = 10^{-7}$) at the cathode cadmium and at the anode oxygen is deposited. Processes at the electrodes are represented by the following equation:

$$\text{anode: } 2\,OH^- = H_2O + \tfrac{1}{2}\,O_2 + 2e;\ \varepsilon_{Pt,O_2\,|\,OH^-} = \varepsilon^{\circ}_{Pt,O_2\,|\,OH^-} - \frac{RT}{2F}\ln\frac{p_{O_2}^{\frac{1}{2}}}{a^2_{OH^-}} =$$

$$= -0{,}401 - \frac{0{,}05915}{2}\log\frac{1}{(10^{-7})^2} = -0{,}814,$$

$$\text{cathode: } Cd^{++} + 2e = Cd;\ \pi_{Cd^{++}\,|\,Cd} = \pi^{\circ}_{Cd^{++}\,|\,Cd} - \frac{RT}{2F}\ln\frac{1}{a_{Cd^{++}}} =$$

$$= -0{,}402 - \frac{0{,}05915}{2}\log\frac{1}{0{,}042} = -0{,}443$$

$$E'_{min} = \varepsilon_{Pt,O_2\,|\,OH^-} + \pi_{Cd^{++}\,|\,Cd} = -0{,}814 - 0{,}443 = -1.257\ V;\ (E_R)_t = 1.257\ V$$

When water is decomposed electrolytically, oxygen is liberated at the anode and hydrogen at the cathode. When the gases escape under pressure of 1 atm., the theoretical decomposition voltage at 25 °C consists of the following potentials at the electrodes:

$$\text{anode: } 2\,OH^- = H_2O + \tfrac{1}{2}\,O_2 + 2e;\ \varepsilon_{Pt,O_2\,|\,OH^-} = \varepsilon^{\circ}_{Pt,O_2\,|\,OH^-} - \frac{RT}{2F}\ln\frac{p_{O_2}^{\frac{1}{2}}}{a^2_{OH^-}} =$$

$$= -0{,}401 + 0{,}05915\log a_{OH^-},$$

$$\text{cathode: } 2\,H^+ + 2e = H_2;\ \pi_{H^+\,|\,H_2,Pt} = -\frac{RT}{2F}\ln\frac{p_{H_2}}{a^2_{H^+}} = 0{,}05915\log a_{H^+},$$

$$E'_{min} = \varepsilon_{Pt,O_2\,|\,OH^-} + \pi_{H^+\,|\,H_2,Pt} = -0{,}401 + 0{,}05915\log a_{H^+}\,a_{OH^-}.$$

By substituting the value of the ionic product of water at 25 °C, $K_v = a_{H^+}\,a_{OH^-} = 1.008 \cdot 10^{-14}$, it follows:

$$E'_{min} = -0{,}401 + 0{,}05915\log 1{,}008 \cdot 10^{-14} = -1.229\ V;\ (E_R)_t = 1.229\ V.$$

Hence all aqueous solutions of acids and bases have the same theoretical decomposition voltage when during electrolysis hydrogen and oxygen are liberated.

2. The measurement of decomposition voltage from the current-voltage curves

For direct measurement of decomposition voltage apparatus illustrated in Fig. 18 is used. Into electrolytic vessel A which is filled with the solution being investigated and provided with a stirrer S to prevent concentration polarization two electrodes E and E' are immersed. The electrodes together with the variable resistance C and a milli-ammeter M are connected in series with the source of direct current B and the terminal voltage is read on the voltmeter V. The method is as follows: Starting from zero the terminal voltage of electrolyzer A is gradually raised by means of variable resistance C. After each rise the current I and the voltage E across the electrodes are recorded. The voltage is raised until a sufficiently strong current flows through the electrolyzer. In order that the result of the measurement obtained is independent of an arbitrarily chosen area of the electrode which affects the nature and velocity of the processes taking place there, the current flowing through the electrolyzer is related to the unit of the electrode area, i. e. it is expressed in current density. This is the ratio of the current in amperes and the effective electrode area in cm^2 or dm^2. The results obtained during measuring the decomposition voltage are usually graphically plotted so that the electrolyzer terminal voltage is plotted on the axis of abscissae and the corresponding current density on the axis of ordinates. A typical example of this current-voltage curve is shown in Fig. 16 (curve *OBD*).

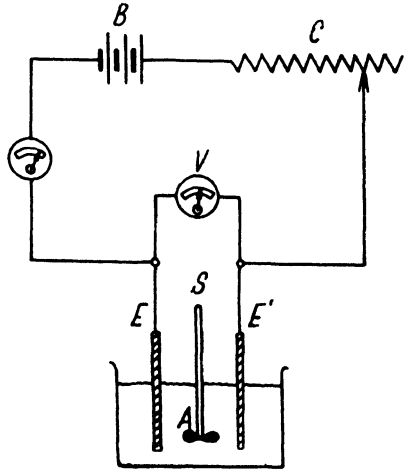


Fig. 18. Apparatus for measurement of decomposition voltage.

As transition between the residual current line *OB* and the line of suddenly increasing current *BD* is not usually sharp, the determination of the decomposition voltage from this diagram presents certain difficulties. It is usually done in such a way that the straight line *BD* is extended and its intersection with the axis of abscissae, i. e. the point E_p is taken for the decomposition voltage; this method of solution is based on the Ohm's law, according to which $E_p = E_R$, when $I = 0$.

The values of decomposition voltage $(E_R)_s$ of some compounds in solution of normal concentration measured by means of platinum electrodes are given in Table 11. For comparison, theoretical decomposition voltages $(E_R)_t$ are also tabulated, calculated by the aforementioned method; the difference

Tab. 11. Decomposition voltage of electrolytes in 1 N - solutions

Electrolyte	Electrolysis products	Decomposition voltage $(E_R)_s$	Theoretical decomposition voltage $(E_R)_t$	$(E_R)_s - (E_R)_t$
HNO_3	$H_2 + O_2$	1,69	1,23	+ 0,46
H_2SO_4	$H_2 + O_2$	1,67	1,23	+ 0,44
H_3PO_4	$H_2 + O_2$	1,70	1,23	+ 0,47
$HClO_4$	$H_2 + O_2$	1,65	1,23	+ 0,42
Na_2SO_4	$H_2 + O_2$	2,21	1,23	+ 0,98
K_2SO_4	$H_2 + O_2$	2,21	1,23	+ 0,98
$NaNO_3$	$H_2 + O_2$	2,15	1,23	+ 0,92
KNO_3	$H_2 + O_2$	2,17	1,23	+ 0,94
$LiNO_3$	$H_2 + O_2$	2,11	1,23	+ 0,88
$Sr(NO_3)_2$	$H_2 + O_2$	2,28	1,23	+ 1,05
$Ca(NO_3)_2$	$H_2 + O_2$	2,11	1,23	+ 0,88
$Ba(NO_3)_2$	$H_2 + O_2$	2,25	1,23	+ 1,02
HCl	$H_2 + Cl_2$	1,31	1,37	0,06
HBr	$H_2 + Br_2$	0,94	1,08	− 0,14
HJ	$H_2 + J_2$	0,52	0,55	− 0,03
$CoCl_2$	$Co + Cl_2$	1,78	1,69	+ 0,09
$ZnBr_2$	$Zn + Br_2$	1,80	1,87	− 0,07
$NiCl_2$	$Ni + Cl_2$	1,85	1,64	+ 0,21
$CdSO_4$	$Cd + O_2$	2,03	1,26	+ 0,77
$CoSO_4$	$Co + O_2$	1,92	1,14	+ 0,78
$CuSO_4$	$Cu + O_2$	1,49	0,51	+ 0,98
$Pb(NO_3)_2$	$Pb + O_2$	1,52	0,96	+ 0,56
$NiSO_4$	$Ni + O_2$	2,09	1,10	+ 0,99
$AgNO_3$	$Ag + O_2$	0,70	0,04	+ 0,66
$ZnSO_4$	$Zn + O_2$	2,55	1,60	+ 0,95

$(E_R)_s - (E_R)_t$ characterizes the irreversibility of the electrode processes.

If we first take compounds which in the course of electrolysis liberate oxygen and hydrogen at the electrodes it will be found that with all of them the decomposition voltage exceeds considerably the theoretically expected value 1.23 V.

The decomposition voltages of acids and bases (HNO_3, H_2SO_4, H_3PO_4, $HClO_4$, NaOH, KOH, NH_4OH) are approximately of the same value, around 1.7 V. It has been proved that the increase in decomposition potential which with all the mentioned compounds is approximately higher by 0.47 V as compared with the theory, is caused primarily by the irreversible nature of the oxygen electrode.

At first sight it would seem that the decomposition voltages of neutral solutions of sulphates and nitrates of alkali metals and alkaline-earth metals should also be in the region of 1.7 V. Actually the respective values are higher.

This is caused by the fact that neutral salt solutions become acid near the anode and alkaline near the cathode (in course of electrolysis of acids or bases the nature of the medium does not change). Therefore, hydrogen is deposited in this case from an alkaline medium, and oxygen from an acid one, whereby the deposition potentials at both electrodes are increased and, thus, the decomposition voltage of the electrolyte also.

Normal solutions of halogen acids (HCl, HBr, HI) are decomposed into elements in the course of the electrolysis as their decomposition voltages are lower then 1.7 V, i. e. the work necessary for decomposition is smaller than with water. By comparing the actual decomposition voltages which are measured at platinum electrodes coated with platinum black, with the theoretically expected values, it can be seen that there is no considerable difference; we may assume, therefore, that both the hydrogen and the halogens are deposited at the electrodes under approximately reversible conditions and that the respective electrodes are nor considerably polarized at weak currents. Since the theoretical decomposition voltage of 1 *N* hydrochloric acid is higher (1.37 V) than that of water (1.23 V), oxygen and not chlorine should be evolved at the anode. The reason why this is not actually so is the higher potential at the oxygen electrode due to overvoltage. When hydrochloric acid undergoes electrolysis for a longer period its decomposition voltage increases proportionally to the falling concentration and at the same time the gas evolved at the anode will show an increased amount of oxygen. If the voltage across the electrolyzer should exceed 1.7 V, the anodically evolved gas will consist of almost pure oxygen.

Halogen acids and some of their salts also (see $CoCl_2$, $ZnBr_2$ in the table) manifest only low polarization. But salts, such as $CdSO_4$, $CuSO_4$, $CoSO_4$, $Pb(NO_3)_2$, $NiSO_4$, $AgNO_3$ etc., show a great difference between the measured and calculated value of the decomposition voltages; this is caused (just as with the acids already mentioned) by the irreversible behavior of the oxygen at the anode.

C. THE ANODE AND CATHODE POTENTIALS DURING ELECTROLYSIS

The decomposition voltage curve gives the relation between the terminal voltage and the current flowing through the electrolyzer. It reproduces simultaneously the changes occurring at both electrodes. For a detailed study of electrolytic processes it is more advantageous to study the potentials at both electrodes separately. For this purpose the equipment illustrated diagrammatically in Fig. 19 is used.

The electrolyzer consisting of the investigated electrode *A* of a known surface area and the auxiliary electrode *B* is connected to the direct current source *C*. The potential of the electrode under observation *A* is measured against a suitable reference electrode (e. g. a calomel one), which is unpolarizable; both

electrodes are connected by means of a salt bridge through a syphon *F*. The end of the syphon glass tube, drawn to a tip, is placed close to the electrode under examination to prevent the simultaneous measurement of the fall of potential in the electrolyte *IR*. The potential across the measured and reference electrodes will then be determined by means of a potentiometer. By changing the resistance *D* the current flowing through the electrolyzer will gradually increase and after each increase and after the current settling at a constant value, the *EMF* in the metering circuit *A*—*G* can be measured on the potentiometer. By subtracting the known potential of the reference half cell from the

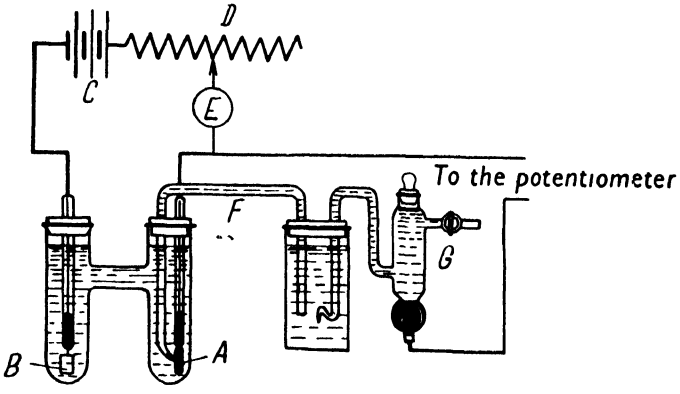


Fig. 19. Measurement of anode and cathode potentials.

found *EMF* value the required potential of electrode *A* will be computed. In this way a series of individual values will be obtained which can finally be plotted in the diagram.

Sometimes the potentials are measured by the commutator method during which the electrolyzing current is suddenly interrupted and the value of the *EMF* of the cell shown by the brief reverse deflection of the voltmeter is quickly read. The voltmeter is connected in an electric circuit parallel with the electrodes. The deflection is caused by products accumulating at the electrodes in the course of electrolysis. The system acts for a short period as a galvanic cell.

Because the electromotive force of this cell falls rapidly after the polarizing current ceases to flow, it is sometimes measured at exact intervals after the circuit is broken. By graphical extrapolation of the obtained values the initial back electromotive force at zero time is found i. e. at the instant of switching off the current. This method is only satisfactory with lower current densities. For higher currents the fall of *EMF* is so rapid that the extrapolation to the moment of a break in the circuit is no longer reliable. For more accurate measurements registration potentiometers are used which automatically register

the potentials at the break of the electrolyzing current. Switching on and off is carried out by an automatic commutator.

We know that the potentials at single electrodes may be quoted either as oxidation or reduction potentials and their values differ in sign only. In modern literature the potentials at the electrodes of galvanic cells are usually recorded as the oxidation potentials (ε), whereas in electrolytic processes an older method using the reduction potential π for denoting the electrode processes is applied; the reversible values of π are calculated according toformula (VI-8).

When electrolysis proceeds under reversible conditions reduction of the cations starts at the cathode at a potential, which is by an infinitely smal value more negative than the equilibrium reduction potential of the system. Analogously the oxidation of ions at the anode (or the dissolution of the anode) begins at a potential, which is by an infinitely small value more positive than the respective equilibrium reduction potential of the system. Actually the value determined experimentally is not always identical with the equilibrium potential. The cathode potentials are usually more negative and the anode potentials more positive than the potentials which agree with the Nernst equation. This is due to the irreversible nature of the respective process (i. e. overvoltage and passivity). These true potentials which are obtained by measuring and at which ions begin to deposit at the electrodes in the form of elements are called deposition (discharge) potentials. When the material of the anode is dissolved in the course of electrolysis the corresponding minimum potential which is needed to start dissolution is called dissolution potential.

When different kinds of ions are in the solution they undergo the electrolytical action of the current at different electrode potentials. Consequently their oxidation or reduction will occur in stages with increasing terminal voltage of the electrolyzer. With regard to the conventional marking of electrolytic potentials the following rules could be derived for the succession of the individual partial processes.

Should the solution contain several cations the cation which has the most positive deposition potential will be discharged first and will be deposited at comparatively lowest voltage across the electrolyzer. With the subsequent fall in concentration of this cation in the solution during electrolysis, the electrode potential will become more negative. As soon as the deposition potential of another kind of cation is attained at the cathode during this fall both metals simultaneously will begin to deposit from the solution. The different kinds of cations are, therefore, discharged in the order, in which the absolute values of their reduction potentials are decreasing. Should the solution contain, e. g. ions Ag^+, Cu^{++} and Zn^{++} with potentials $\pi_K = +0.80$, $+0.34$ and -0.76 V, first silver, then copper and lastly zinc will be deposited at the cathode.

On the other hand the succession of the processes proceeding at the anode (e. g. dissolution of metals or discharging of anions) will follow the order, in which the absolute values of their reduction potentials will increase. Thus e. g. at the copper anode, dipped into the acidified solution of copper sulphate,

copper will be dissolved according to the equation $Cu = Cu^{++} + 2e$, since the potential $\pi_A = + 0.34$ V, which this process has, is less positive than the deposition potential of oxygen ($\pi_A = + 1.68$ V). If the copper electrode should be replaced by a platinum one oxygen will be deposited from the solution at the anode, as in this case no other process proceeding at a lower potential would be possible.

The current curves, illustrating the relation between the cathode or anode potentials and the current density, have usually the shape indicated in Fig. 20. In the diagram the course of the cathode potential is illustrated on the left

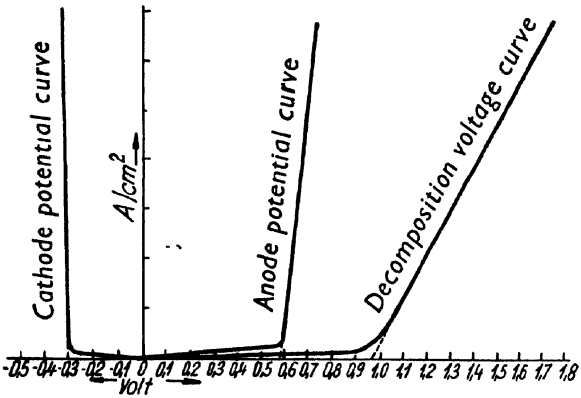


Fig. 20. The relation between the cathode or anode potential and the current density.

and that of the anode one on the right. For comparison the curve representing the decomposition voltage E_R is also plotted in the same diagram; its abscissae are giving the total voltage across the electrodes including the potential difference which is necessary to overcome the ohmic resistance of the electrolyte. The values of deposition potentials at the anode or cathode can be determined from the current curves by a similar extrapolation by which the decomposition voltage is determined and the data obtained could be then compared with the equilibrium potentials.

Since in the course of measurement of the anode and cathode potentials the influence of the electrolyte resistance is eliminated the current curves during the ideal reversible course of the electrolysis should rise vertically upwards after transgressing the cathode or anode equilibrium potentials. Actually, however, this is never exactly the case as electrolysis is always accompanied by polarization phenomena, at least by concentration polarization. Owing to this polarization the rising parts of the current curves are always somewhat inclined to the voltage axis. From the magnitude of their slope it can be found

to what extent the irreversible processes occur in the course of electrolysis. Since the rising part of the cathode potential curve is usually less inclined to the axis of abscissae than that of the anode potential curve, the cathodic process approaches more the reversible course than the anodic one.

D. POLARIZATION

In this chapter more detailed attention will be paid to the potential changes at the electrodes which occur when an appreciable current flows through the electrolyzer. Such changes are due to some processes which cannot proceed with the velocity required by the current density applied.

According to the reasons causing these electrode potential changes we distinguish between concentration polarization and irreversible polarization phenomena; among the latter are included overvoltage and passivity. All these phenomena increase the back electromotive force in the course of electrolysis which acts against the voltage of the electrolysing current (see formula VII-1). To compensate this back *EMF* it is necessary to apply a higher voltage of the current source and this will increase the energy consumption for the electrolysis. Since expenditure on electric energy is one of the most important when calculating the overall cost of electrochemical products the greatest possible attention is paid to the problem of maintaining the electrode potentials as low as possible.

Electrolysis with a dropping mercury electrode, invented by *J. Heyrovský*, on which the well known polarographic method is based, enables a detailed investigation of polarization processes as well as the study of electrode processes from the point of view of kinetics, reversibility, adsorption and capacity phenomena.

1. Concentration polarization

Concentration polarization is a phenomenon common to all electrolytical processes. As long as abnormally high current densities or too diluted solutions are not applied, this kind of polarization will not occur to a considerable extent in industrial electrolyses. This is due to the fact that the concentration differences which initiate this kind of polarization are usually not too high.

The cause of concentration polarization is the slow rate of diffusion of ions which cannot counterbalance the concentration variations in the close proximity of both electrodes arising from the discharge or formation of ions. Let us imagine, e. g. the electrolysis of a silver nitrate solution between two silver electrodes. When no current is flowing through the system the potentials at both electrodes are of the same value and are mutually compensated. As soon as electrolysis starts, the concentration of Ag^+ ions will begin to rise owing to the dissolution of silver at the anode; on the contrary the concentration of these ions round the cathode will fall because the deposition of metallic silver will here take place. The concentration differences produced will never be fully compensated

for by diffusion or by migration. Therefore, as follows from the Nernst law, the equilibrium electrode potential as shown in a currentless state against the given solution will become more negative at the cathode by the absolute difference $\Delta\pi_K$, and more positive at the anode by the absolute difference $\Delta\pi_A$. The values $\Delta\pi_K$ and $\Delta\pi_A$ are considered the measure of concentration polarization at the anode and cathode; added together they will give the magnitude of the resulting back electromotive force $E_p = \Delta\pi_K + \Delta\pi_A$, which acts against the electrolyzing voltage. Should electrolysis be interrupted and the polarized cell short circuited, the current will flow in the direction opposite to the electrolyzing current until the concentration differences round the electrodes are equalized.

a) *Concentration polarization at the cathode.*

If the rate of diffusion was sufficiently great under any circumstances the ions discharged at the cathode could be replaced there at the rate required and the cation activity would in this case be maintained at the electrode at the same level as in the bulk of the solution. Under such conditions a current of arbitrary magnitude may flow through the electrode at the equilibrium or only at an infinitely more negative potential the value π of which would depend on the activity a of electromotively active ions in the electrolyte:

$$\pi = \pi^\circ + \frac{RT}{nF} \ln a. \qquad \text{(VII-6)}$$

Actually, however, diffusion is not capable of replacing at the same rate the amount of ions discharged at the cathode, at the constant external voltage across the cell, therefore, the activity of the ions in the close vicinity of the electrode drops, until the constant value a_c is attained after reaching a stationary state. Assuming that the electrode reacts quickly to the concentration changes in the surroundings, its initial potential π will be changed into π_c:

$$\pi_c = \pi^\circ + \frac{RT}{nF} \ln a_c. \qquad \text{(VII-7)}$$

When the ionic activity (a) is not changed in the bulk of the solution, the absolute value of concentration polarization at the cathode $\Delta\pi_K$ is expressed by the difference of the potentials π and π_c, hence:

$$\Delta\pi_K = \pi - \pi_c = \frac{RT}{nF} \ln \frac{a}{a_c}. \qquad \text{(VII-8)}$$

In the stationary state the rate of diffusion will be equal to the rate of discharge of the ions by the current. In general, also the ions must be taken into consideration which are brought up to the electrode by migration, hence increasing the amount of ions reaching the cathode in a time unit.

The amount of cations transported by diffusion only will be calculated

according to Fick's law of diffusion. To this end the distribution of concentrations in the electrolyte, schematically illustrated in Fig. 21, must be noted. It is evident that the electrolyte concentration C in the bulk of the solution (with corresponding activity a) falls in the direction to the electrode, according to the curve CBA; the lowest concentration c_c (with activity a_c) is closely round the cathode. It is understood that the ions diffuse in that part of the solution between the electrode and point C, while the concentration gradient decreases in proportion to the distance from the cathode. To simplify the calculation, this variable concentration gradient is replaced by an equivalent linear gradient

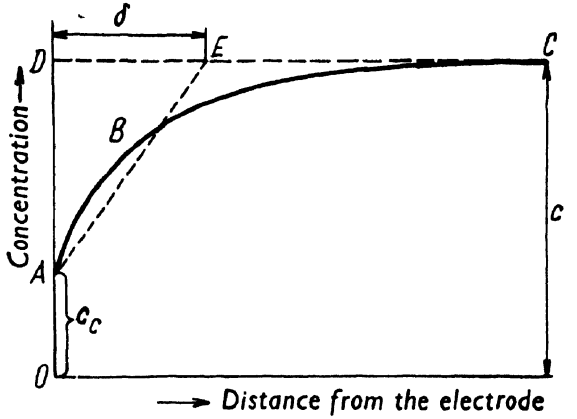


Fig. 21. The diffusion layer at the electrode surface.

AE, and the distance $DE = \delta$ is taken as the thickness of the hypothetical layer across which the diffusion takes place.

According to measurement results the thickness of the hypothetical diffusion layer with unstirred aqueous solutions at 20 °C is approximately 0.5 mm. When agitating the liquid the thickness of the layer is diminished to 0.01 to 0.05 mm, according to the shape of the stirring device and its revolutions.

If A is the effective surface area of the electrode and D the diffusion coefficient of ion, then the quantity of ions m_1 diffusing through the layer of the thickness δ, in one second, at activity difference $(a - a_c)$, according to Fick, will be expressed by the equation:

$$m_1 = \frac{AD}{\delta}(a - a_c)\text{ *) gram-ions of the cation.} \qquad \text{(VII-9)}$$

*) The Fick's Law of diffusion in its original form had concentrations. It is, however, more accurate to express this law using activities, as the diffusion depends obviously on the free energy difference between the more concentrated and more diluted solutions.

The number of ions transported to the electrode by migration can be calculated as follows: the quantity of electricity of 1 faraday carries to the cathode t_+ gram-equivalents, i. e. t_+/n gram-ions, of the cation. The current I carries then per second:

$$m_2 = \frac{It_+}{nF} \text{ gram-ions of the cation.} \qquad \text{(VII-10)}$$

The total number of gram-ions of the cation $m = m_1 + m_2$ transported per second to the cathode by diffusion and migration will then determine the current I, passing through the electrode at the cathode potential π_c:

$$m = \frac{I}{nF} = \frac{AD}{\delta}(a - a_c) + \frac{It_+}{nF}. \qquad \text{(VII-11)}$$

Substituting into this equation*) the current density I_h for the ratio I/A and for $(1 - t_+) = t$, i. e. total of the transference numbers of all other ions present in the diffusion layer, except the one being discharged, then

$$I_h = \frac{nDF}{t\delta}(a - a_c). \qquad \text{(VII-12)}$$

If

$$k = \frac{nDF}{t\delta}, \qquad \text{(VII-13)}$$

the following equation is valid for the relation between activities and the current density:

$$a_c = a - \frac{I_h}{k}. \qquad \text{(VII-14)}$$

Substituting now this expression into equation (VII-8), the following equation will be obtained:

$$\Delta\pi_K = \frac{RT}{nF} \ln \frac{ka}{ka - I_h}. \qquad \text{(VII-15)}$$

From this equation it can be seen that the concentration polarization will be smaller with an increased concentration (activity) of ions in the solution at a given current density. Its value can also be decreased by increasing the term $k = nDF/T\delta$. This can be achieved either by the application of higher temperature (the diffusion coefficient increases in proportion to the temperature), or by agitating the solution which would reduce the thickness of the diffusion layer. Concentration polarization can be reduced by agitating, but not comple-

*) When an indifferent electrolyte, transferring the entire current is added in excess to the solution (e. g. potassium nitrate to the silver nitrate solution), the second term of the equation (VII-11) equals zero, or the quantity t in the equation (VII-12) equals unity.

tely eliminated because even at the most intensive movement of the solution a thin layer of stationary liquid will remain in the immediate vicinity of the electrodes.

When plotting the relation between concentration polarization and current density the resultant curve will be of the form, illustrated in Fig. 22. The curve starts to move upwards at point A which gives the value of the equilibrium potential (see equation (VII-15) for $I_h = 0$). Proportionally with increased current density the cathode potential increases almost linearly at the beginning, later it increases more rapidly, until finally the curve at point B breaks into

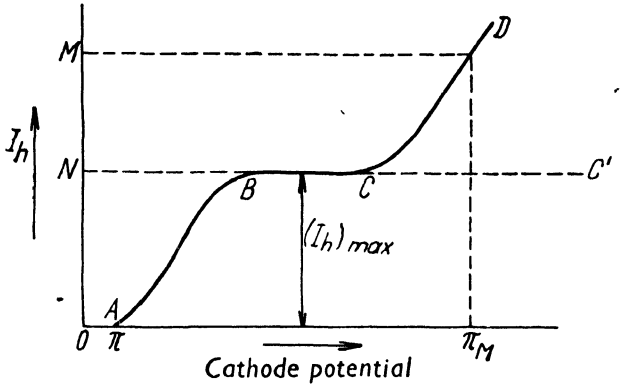


Fig. 22. Relation between concentration polarization and current density.

a horizontal line (BC). This means that the current density attained its maximum value $(I_h)_{max}$ and further on is independent of the cathodic polarization. From the equation (VII-15) we can see that this state will be attained when the current density reaches the value of the product ka. The maximum current density $(I_h)_{max}$, known as the limiting current density, can be calculated if into the formula $(I_h)_{max} = ka$ we substitute for the constant k the expression from equation (VII-13):

$$(I_h)_{max} = \frac{nDF}{t\delta} a. \qquad \text{(VII-16)}$$

From this equation it can be seen that the limiting current density will be higher at higher solution concentration (a), at more vigorous agitation of the solution (lower δ) and at higher temperature (higher D).

If we compare equations (VII-16) and (VII-12) we see that after the limiting current density is attained the activity of the ions at the cathode will drop to zero ($a_c = 0$); under these conditions the rate of the diffusion of ions to the electrode attains its maximum and all the ions transported to the electrode are discharged instantaneously. With a further increase in the terminal voltage

the current passing through the electrolyzer will not increase within the limits *BC*, as the number of ions transported to the electrode per second after exceeding the limiting current density will remain constant.

b) *Concentration polarization at the anode*

Concentration polarization which accompanies the dissolution of the metal at the anode is, in many respects similar to that at the cathode. It is, however, manifested to a much lesser extent. Since in the given instance the concentration of ions at the electrode is higher than in the bulk of the solution ($a_c > a$), the sign of the activities in equation (VII-14) has to be reversed:

$$a_c = a + \frac{I_h}{k}. \tag{VII-17}$$

The absolute value of the concentration polarization at the anode is determined by the difference of the anodic potential π_c at a flow of current and the equilibrium potential without a current flow. By application of the general formulae (VII-6) and (VII-7) the following equation will be obtained:

$$\Delta\pi_A = \pi_c - \pi = \frac{RT}{nF} \ln \frac{a_c}{a}. \tag{VII-18}$$

By substituting the equation (VII-17) into that formula it will follow

$$\Delta\pi_A = \frac{RT}{nF} \ln \frac{ka + I_h}{ka}, \tag{VII-19}$$

which expresses the relation between the concentration polarization at the soluble anode and the current density.

Let us now assume that the system is composed of two identical metal electrodes dipped into the same electrolyte, in which the metal at the anode is dissolved and deposited at the cathode. When working under conditions at which the limiting current density is obtained at the cathode the current flowing through the system is $(I_h)_{max} = ka$. If the diffusion layers at both electrodes are of the same thickness (i. e. the constant k is of the same magnitude), this relation can be substituted into the formula (VII-19) and the polarization potential at the anode be calculated:

$$\Delta\pi_A = \frac{RT}{2F} \ln \frac{2ka}{ka} = \frac{RT}{2F} \ln 2. \tag{VII-20}$$

Polarization at the anode is in this case comparatively very small; on the contrary the concentration polarization at the cathode could, in theory, attain values of unlimited magnitude.

Should a fully unpolarizable electrode be applied as a cathode which did not limit in any way the passage of current the anode could be dissolved at a current density of any magnitude, according to formula (VII-19). But what happens

is that the solution surrounding the anode sooner or later becomes saturated by the salt produced which separates from the solution at the electrode and so diminishes its effective area and increases the effective current density. In this way the characteristic properties of the electrode are completely changed and the anode becomes passive.

The phenomenon of limiting current can appear at anodes as well as at cathodes. When an indifferent electrode is immersed into a solution of ferrous salt or any other anodically oxidizable substance the limiting current density will be attained at a certain terminal voltage. The limiting current density will depend not only on the maximum number of ions (Fe^{++}) transferred by diffusion or even migration in a unit of time from the bulk of the solution to the electrode but also on the maximum transport-rate of the products (Fe^{+++}) in the opposite direction.

c) *Simultaneous deposition of several kinds of ions*

Let us return to the processes at the cathode and to the limiting current. According to equation (VII-15) concentration polarization should attain infinite value as soon as the current density reaches the limit value (see the dashed part of the curve CC' in Fig. 22.). This condition cannot occur because there are other kinds of ions present in the solution the deposition of which is more difficult. For instance hydrogen ions formed by dissociation of water start to discharge as soon as the cathode potential rises up to a value necessary for hydrogen deposition. At that moment (C) the horizontal section BC of the curve corresponding to a limiting current turns upwards to form an ascending branch corresponding to deposition of another kind of ions.

As it will be seen from the abovementioned figure, at lower potentials corresponding to AB only cation M_1+ is deposited from the solution, until the range of limiting current BC is reached. In the course of further cathodic polarization the potential of the electrode rises up to the value C which marks the beginning of the deposition of other ions M_2^+. From this moment on both kinds of ions are deposited simultaneously. The branch CD is actually a new curve $\pi - I_h$ and is related to a more difficult deposition of the other ion while the corresponding potential π_{M_2}/M_2+ is determined by that part of current density, which lies above the range of the limiting current. If for instance the total current density at cathode potential π_M is M, then the section ON of the ordinate represents the relative part of current used for deposition of M_1^+ ions and the section NM the current used for depositing ions M_2^+.

The abovementioned phenomenon — encountered rather frequently in the case of a low concentration of ions M_1^+ in the solution — can be observed for instance during the course of depositing metals from aqueous solutions. In such solutions also hydrogen ions are present which have been formed by dissociation of water. Should the current density exceed the limit value of the metal ions discharge gaseous hydrogen will be deposited at the cathode with increased rate simultaneously with the metal.

At current densities corresponding to the curve *ABC* the deposition of metal is the only process which consumes the whole quantity of the current passing through the cell; the current efficiency within this range, therefore, equals hundred per cent. At current densities above the limiting current the electrolysis along the curve *CD* actually comprises two electrolytical processes; so only a part of the current is used for the required process and as a result the current efficiency drops below 100 per cent.

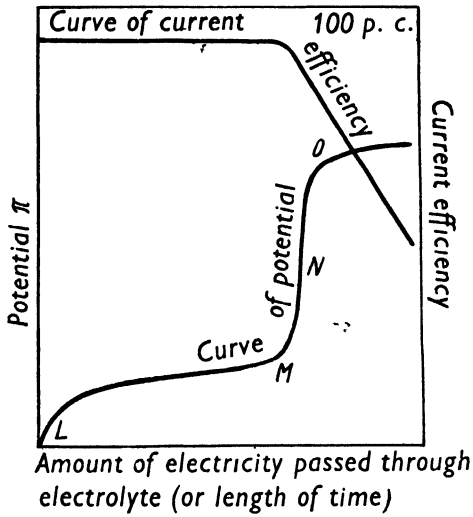


Fig. 23. Course of potential and current efficiency related to the amount of electricity passed through the electrolytic cell during a prolonged electrolysis.

If any cation can exist in several states of oxidation its reduction at the cathode may be accompanied by several limiting currents. For instance, if for the reduction of vanadic acid dissolved in concentrated sulphuric acid platinum electrode coated with platinum black is used, three steps in the reduction process can be easily distinguished, namely $V^{V} \rightarrow V^{IV}$, then $V^{IV} \rightarrow V^{III}$, and finally the stage of hydrogen liberation.

Analogously to the processes at the cathode, oxidation at the anode takes place in the course of reversible processes in which the phenomenon of limiting current can be observed. Ions of bivalent iron can be anodically oxidized with a current efficiency of 100 p. c., if the density of the current used does not exceed the value of the limiting current; above this value also oxygen is liberated from the solution.

In all hitherto discussed instances the potentials at which the secondary process occurs, such as the liberation of hydrogen, oxygen or chlorine, were widely different from the potentials corresponding to the primary oxidation or reduction process. Sometimes this is not the case. The reduction potential of reaction $Sn^{IV} \rightarrow Sn^{II}$, for example, is so close to the potential of hydrogen deposition that both processes take place even at comparatively low current densities.

Up to now it has been assumed that the concentration of the bulk of the solution remains practically constant with increasing current density. Actually the concentration of the active substance drops during the course of every electrolytical reduction and oxidation. It is, therefore, advantageous to study the electrochemical process at a constant current density and to follow the relation between potentials and current efficiencies and quantities of electric-

ity passed through the electrolyzer (see Fig. 23). Let us now consider cathodic deposition of copper from its solution with a current density which is lower than the limit value corresponding to the initial concentration of Cu^{++} ions. On switching the current the potential of the cathode corresponds to the current density used at the initial concentration of the electrolyte. In the course of electrolysis the concentration of the active substance in the solution drops and while the current density is kept constant the potential becomes gradually more negative along the $L\,M$ branch. As soon as the potential attains the value corresponding to the position of point M, it indicates that the solution is depleted of Cu^{++} ions to such an extent that the current density used is just equal to the limiting density. In the course of further electrolysis the concentration of Cu^{++} ions is no longer sufficient for the existing current density to be maintained; therefore, the potential of the cathode quickly rises (in direction of negative values) till it attains at point O the potential of deposition of another cation (e. g hydrogen). From then on both ions are discharged simultaneously.

In the further course of electrolysis the concentration of Cu^{++} in the solution drops still more so that the quantity of copper deposited at the cathode per unit time is also reduced. If at the same time the current density is to remain constant the evolution of hydrogen will consume more and more current with ensuing rise of the cathode potential, which, however, now increases at a slower rate. At potentials corresponding to the part LMO of the curve the deposition of copper at the cathode is the sole process so that current efficiencies within this range equal 100 per cent. As soon as the potential rises during electrolysis to the value corresponding to point O, the current efficiency starts to drop as a steadily increasing amount of hydrogen apart from copper is also deposited.

The curves plotted in Fig. 23 are valid for reversible oxidation and reduction processes; similar relations may be observed in some irreversible processes proceeding with high velocities.

2. Overvoltage

The deposition potentials of most metallic ions are practically the same as the equilibrium potentials of corresponding electrodes. In case of other metals, however, (such as nickel, iron, cobalt, and even copper), and mainly in the case of gases the potential necessary for the discharge of ions is as a rule much higher. The difference between the actual deposition potential and its equilibrium value is denominated as overvoltage. While concentration polarization can be ascribed to insufficiently quick equalization of concentrations at the electrodes the overvoltage is caused by the slowness of some rate-determining individual step in the total electrochemical reaction of ions. The significance of overvoltage in industrial practice is really far reaching, as this phenomenon makes many processes possible. On the other hand its existence may prove undesirable in some cases because the terminal voltage necessary for accom-

plishing the electrolytic process is thus raised whereby the consumption of electrical energy will also increase.

a) *Overvoltage associated with electrolytic evolution of hydrogen*

The systematic investigation of the phenomenon of overvoltage was initiated by *Caspari's* study of potentials at which first hydrogen and oxygen bubbles appear at electrodes made of different materials during the electrolysis of water. To distinguish between the overvoltage observed on the passage of a current of greater density through an electrolytic cell and the overvoltage measured by Caspari, the latter phenomenon is denominated minimum overvoltage. Table 12 comprises some values of minimum hydrogen overvoltage found by Caspari at different cathodes in solution of N—H_2SO_4.

Tab. 12. Hydrogen overvoltage at different metals

Electrode	Hydrogen overvoltage in volts	Electrode	Hydrogen overvoltage in volts
Platinum coated with platinum black (platinized)	~ 0,0	Copper	0,23
Palladium	~ 0,0	Cadmium	0,48
Gold	0,02	Tin	0,53
Smooth platinum	0,09	Lead	0,64
Silver	0,15	Zinc	0,70
Nickel	0,21	Mercury	0,78

These values are not accurate and cannot be reproduced in a reliable manner. It is due to the fact that apart from the easily definable factors (such as current density, material of electrodes, temperature, pressure etc.) the overvoltage also depends to a great degree on factors that cannot be controlled so easily i. e. on the state of the electrode surface, way of the mechanical treatment of the same, its past (i. e. whether it had been polarized beforehand or not); even traces of impurities prove important. The difficulties connected with the definition of surface properties of electrodes are aggravated by the variability of the overvoltage in the very course of electrolysis.

As measurement of minimum overvoltage is marked by an inherent error due to indefinable and thus problematic determination of the beginning of a visible evolution of gases, it is more exact to quote the values which are valid for a certain current density (see Tab. 13a, b).

In Fig. 24 there is a graphical representation of the dependence of hydrogen overvoltage — on electrolyzing 2N—H_2SO_4 at 12 °C — upon current densities on several metals.

The platinized platinum (platinum coated with platinum black) is the only

Table 13a. Overvoltage of hydrogen deposited from solution of $2N-H_2SO_4$ at 20 °C at some metals

Electrode	Overvoltage in V at current densities of mA/sq.cm.						
	1	10	50	100	500	1000	1500
Platinum coated with platinum black (platinized)	0,015	0,030	0,038	0,041	0,045	0,048	0,050
Smooth platinum	0,024	0,068	0,186	0,288	0,573	0,676	0,768
Gold	0,241	0,390	0,507	0,588	0,770	0,798	0,807
Copper	0,479	0,584	—	0,801	1,186	1,254	1,269
Graphite	0,560	0,779	0,903	0,977	1,171	1,220	1,221
Bismuth	0,780	1,050	1,150	1,140	1,210	1,230	1,290
Cadmium	0,981	1,134	1,211	1,216	1,246	1,254	1,257
Lead	0,520	1,090	1,168	1,179	1,235	1,262	1,290
Tin	0,856	1,077	1,185	1,223	1,238	1,231	1,229
Zinc	0,716	0,746	0,926	1,064	1,201	1,229	1,243
Nickel	0,563	0,747	0,890	1,048	1,208	1,241	1,254
Iron	0,404	0,557	0,700	0,818	1,256	1,292	1,291
Silver	0,475	0,762	0,830	0,875	1,030	0,089	1,084
Aluminium	0,565	0,826	0,968	0,996	1,237	1,286	1,292

Table 13b. Hydrogen overvoltage in $2N-H_2SO_4$ at 25 °C on mercury and palladium

Current density in mA/sq.cm	Overvoltage on mercury in V	Current density in mA/sq.cm	Overvoltage on palladium in V
0,0	0,281	0,0	—
0,077	0,556	0,227	0,055
0,769	0,849	1,135	0,139
1,54	0,930	2,27	0,182
3,87	1,006	4,54	0,235
7,69	1,036	11,35	0,317
38,7	1,063	22,7	0,403
76,9	1,067	113,5	0,721
154	1,075	227	0,861
387	1,105	454	0,952
769	1,108	1135	1,051
1153	1,126	2270	1,117

metal at which hydrogen is deposited at zero current density or at current densities sufficiently low without any overvoltage, i. e. reversibly. At higher current densities an overvoltage on the platinum begins to manifest itself yet its value remains rather low. On the other hand hydrogen overvoltage on smooth platinum never equals zero, not even at zero current density; at higher current densities it increases at a comparatively great rate. In the case of gold, palladium

and graphite it is also possible to observe a great increase of the overvoltage, the initial values of which are comparatively small. On the other hand such metals as mercury, bismuth, cadmium, lead, zinc, nickel, iron and silver manifest a high overvoltage even at low current densities; this overvoltage rises quickly at first, as the current density is increased, while later its value remains practically constant.

The dependence of hydrogen overvoltage ω on current density is expressed by the formula:

$$\omega = a + b \log I_h \qquad \text{(VII-21)}$$

where a and b are constant at a given temperature.

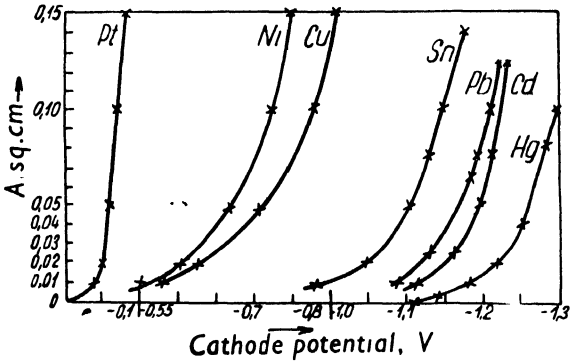


Fig. 24. Overvoltage of hydrogen evolved from 2N – H_2SO_4 at 12 °C on different electrodes.

Whilst a is a constant characteristic for individual metals, b is according to experimental results approximately of the same value at a given temperature for a variety of metals. Its approximate magnitude at 25 °C is $b = 0{,}12$. Moreover it was found that the constant b increases linearly with temperature in accordance with the equation:

$$b = 2\,\frac{2.3\,RT}{F}. \qquad \text{(VII-22)}$$

The relations expressed by equations (VII-21) and (VII-22) are valid for overvoltage at mercury, silver, palladium, aluminium, copper and gold at current densities ranging from 10^{-6} to 10^{-1} A/sq. cm. Other metals show different behavior. So, for instance, for graphite and lead values of b up to 0.3 have been measured whilst for platinized platinum the unusually low value of $b = 0.025$ has been found, which increases with time; in case of smooth platinum the growth of the constant from the value 0.075 to 0.19 with time has been also observed.

It has already been mentioned that the magnitude of overvoltage depends on the state of the electrode surface. If the surface is rough overvoltage is lower than it would be at a smooth electrode at the same current density. This drop of overvoltage, especially evident in case of platinum, can be probably explained by an increase of the effective surface of the electrode whereby effective current density is lowered. On increasing the temperature, overvoltage drops at a rate of some 2 mV per degree. Pressure has an analogous effect whereby overvoltage drops some 0.04 V on increasing the pressure by 10 atm. It is not yet reliably known to which degree overvoltage is influenced by the concentration of hydrogen ions; it seems, however, that the overvoltage is independent of the pH. Great difficulty is encountered when measuring overvoltage because it changes with time what indicates a likely change in the nature of the surface. There is another complication, namely, that the overvoltage reacts sensitively to the presence of even the smallest traces of impurities contained in the material of the electrodes which also contributes to the imperfect reproducibility of the measured values.

With such a great number of effects, and some of them very difficult to identify, it is not surprising that many hypotheses have been proposed to explain the phenomenon of overvoltage. All these theories agree in one respect only and that is that overvoltage is caused by a certain partial stage in the overall reaction which due to unsufficient velocity cannot satisfy the requirements of the current density used; as a result the intermediate product of this transient stage accumulates at some spot of the electrode and gives rise to an electrical double layer with a certain potential across it. To overcome this potential which is a sort of energetical barrier it is necessary to increase the cathode potential just by the value of the overvoltage so that a current of the required density can flow through the electrodes.

When hydrogen ions are discharged the following individual steps may be considered:

a) diffusion of hydroxonium ions H_3O^+ from the solution to the cathode;

b) transfer of H_3O^+ ions from the solution onto the cathode;

c) discharge of H_3O^+ ions and formation of atomic hydrogen after receiving one electron;

d) combination of hydrogen atoms to form molecular hydrogen;

e) liberation of molecular hydrogen from the surface of the electrode.

If all these reaction steps could take place with sufficient velocity on the electrodes the deposition of hydrogen would be a reversible process. If, however, one or several of these processes do not proceed with sufficient velocity the equilibrium cannot be maintained at every moment of the reaction and irreversibility results which causes overvoltage.

Several hypotheses have been worked out in the course of time that try to explain the reason for hydrogen overvoltage by the slowness of this or that partial process taking place during the discharge of hydrogen cations. The

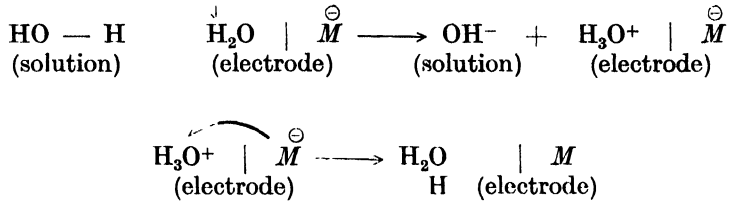
analysis of all former theories of overvoltage, today acknowledged as superseded is beyond the scope of this work, we shall therefore, confine ourselves to the explanation given by *Tafel*, which was nearly generally accepted at one time. According to his hypothesis overvoltage is caused by the slowness of the process *d* (as mentioned previously) i. e. of the reaction:

$$2H \text{ (adsorbed or dissolved in metal)} = H_2 \text{ (adsorbed)}.$$

The difference between the values of hydrogen overvoltage at different electrodes is ascribed by Tafel to a different catalytic effect of individual metals upon the rate of combination of hydrogen atoms to give molecules. Metals with a low hydrogen overvoltage (e. g. Pt and Pd) act according to this theory as efficient catalysts while metals with a high overvoltage (Pb, Hg, Sn, Cd) behave as poor catalysts. Tafel based this theory on observations according to which the rate of combination of atomic hydrogen on the surface of different metals drops in the following order: Pt, Pd, Fe, Ag, Cu, Pb and Hg. His theory was also supported by the fact that the best catalyst for hydrogenation, where reaction $H_2 \rightarrow 2H$ is probably the first stage, are those metals which have a low hydrogen overvoltage. If these metals catalyze hydrogenation it is evident that they can accelerate also the reversed process.

Tafel's theory leads to the conclusion that the slope of the straight line representing the dependence of the overvoltage on current density at constant temperature is given by the expression $b = \frac{2.3RT}{2F}$, instead of the quadruple of that value ascertained for most metals. In this respect Tafel's theory does not agree with experiment. It seems, therefore, that this theory applies only to metals with exceptionally low hydrogen overvoltage, such as, platinized platinum where the constant *b* is approximately equal to the value as postulated by Tafel.

Among modern conceptions it is necessary to emphasize the explanation of *Eyring*, *Glasstone* and *Laidler* according to which the cause of overvoltage is to be found in the insufficient rapidity of transfer of protons, i. e. non-solvated hydrogen ions, from the solution onto the electrode. These authors assume that the protons do not originate from hydrogen ions present in the solution but from molecules of water. According to their conception an electrode submerged in aqueous solution is covered by a molecular layer of adsorbed molecules of water with adjacent further molecules of water that are already part of the main body of the solution. Under the effect of the terminal voltage of the electrolyzer protons are transferred from molecules of water in the solution to molecules adsorbed on the surface of the electrode. As a result hydroxyl ions remain in the solution while hydroxonium ions formed on the surface of the electrode readily receive one electron, thus changing into atomic hydrogen. The mechanism of this process can be represented by a scheme where *M* marks the electrode and shows that there are free electrons available on the electrode:



The first of the processes indicated is a slow one, and this is the cause of overvoltage; the other process is more rapid. The slowness of the transfer of the proton is due to the existence of the energetical barrier a proton has to overcome before arriving from the solution onto the electrode.

On treating their hypothesis mathematically the authors arrive at equation (VII-21) where for the constant b a value is found which agrees well with observation results with most metals. Their explanation also allows for the dependence of overvoltage upon the material of the cathode as a logical consequence of the theory. In case the material of the electrode (such as Pt, Pd, Au, Fe) adsorbs hydrogen easily, it means that relatively strong bonds of the type M—H arise which facilitate the transfer of protons from the solution onto the electrode, so that a comparatively low voltage is sufficient to overcome the energetical barrier. On the other hand such metals as mercury, tin or lead, of low adsorption ability with respect to hydrogen, belong duly among the metals with a high hydrogen overvoltage.

J. Heyrovský bases his explanation of the mechanism of hydrogen deposition on a polarographic study of hydrogen overvoltage at the dropping mercury cathode; he assumes it to be the result of three successive reactions:

a) $H_3O^+ + e = H + H_2O$

b) $H + H_3O^+ = H_2^+ + H_2O$

c) $H^+_2 + e = H_2$

While according to this theory the reactions a) and c) are very quick, the resulting rate of the whole electrode process is determined by the second reaction, b), the slowest one.

b) *Oxygen overvoltage*

Overvoltage associated with the evolution of oxygen at the anode is even less reproducible than the hydrogen overvoltage because of its greater variability with time and because of the formation of metal oxides on the surface of the anode. Approximate values of minimum overvoltage as measured by Caspari on oxygen evolved from a normal NaOH solution at 25 °C at different metals are contained in Table 14.

According to this table there is no metal at which oxygen could be deposite reversibly, i. e. without overvoltage. With increasing current load the over

Table 14. Overvoltage of oxygen evolved from a normal solution of NaOH at 25 °C on various metals

Electrode	Oxygen overvoltage in V	Electrode	Oxygen overvoltage in V
Nickel	0,06	Cadmium	0,43
Cobalt	0,14	Palladium	0,43
Platinized platinum	0,25	Smooth platinum	0,45
Lead	0,31	Gold	0,53
Silver	0,41		

Table 15. Overvoltage of oxygen evolved from a normal KOH solution at 25 °C

Electrode	Overvoltage at current density of mA/sq.cm in volts						
	1	10	50	100	500	1000	1500
Platinized platinum	0,40	0,52	0,61	0,64	0,71	0,77	0,79
Smooth platinum	0,72	0,85	1,16	1,28	1,43	1,49	1,38
Gold	0,67	0,96	1,06	1,24	1,53	1,63	1,68
Copper	0,42	0,58	0,64	0,66	0,74	0,79	0,84
Graphite	0,53	0,90	—	1,09	1,19	1,24	1,28
Nickel	0,35	0,52	0,67	0,73	0,82	0,85	0,87
Silver	0,58	0,73	0,91	0,98	1,08	1,13	1,14

voltage on all metals rises, too, as well as on graphite (see Table 15 and Fig. 25).

It is interesting that oxygen overvoltage on platinum and gold is higher than on nickel and copper which is the very opposite to what has been observed in the case of hydrogen overvoltage. Otherwise they both manifest themselves in much the same manner. So for instance the oxygen overvoltage also drops with increasing temperature and rises with increasing current density. Another point of agreement is that the overvoltage of oxygen deposited from acid solution is very probably independent of pH which does not hold good for alkaline solution.

According to another conception, valid until recently, the oxygen evolves at the anode by decomposition of intermediary and unstable higher oxides, such as $Pt\,O_3$ and $Pt\,O_4$ in the case of platinum, Ni_2O_3 and $Ni\,O_2$ in the case of nickel, and Cu_2O_3 and $Cu\,O_2$ in the case of copper; these oxides were considered to be the cause of the overvoltage. Although the existence of these oxides which bring about a back electromotive force that manifests itself as soon as the electrolyzing current is interrupted, cannot be denied, it seems athe r doubtful today whether they would be the real cause of the overvoltage.

Even if we admit that the anode potential measured at rather high current density really agrees with the potential of the higher oxide formed by reaction of the metals with the active oxygen, the question still remains why no oxygen starts to be evolved already at a lower, reversible potential. Even other theories, according to which overvoltage is ascribed to an accumulation of atomic oxygen in the electrode or to a low velocity of its combination to the molecular form, do not explain satisfactorily all phenomena encountered on anodic deposition of oxygen.

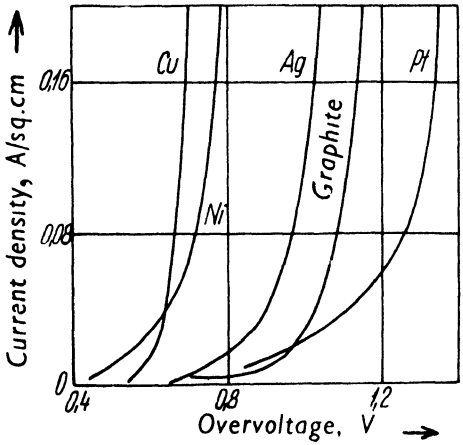


Fig. 25. Overvoltage of oxygen evolved from a normal solution of KOH at room temperature on different anodes.

The analogy between oxygen and hydrogen type of overvoltage gave *Eyring*, *Glasstone* and *Laidler* an idea to explain both phenomena by the same theory, i. e. to ascribe the occurrence of overvoltage to the insufficient velocity by which protons are transferred across the energetical barrier at the electrode. The only difference is, that in the case of oxygen overvoltage the protons are not transferred from molecules of water in the solution toward the molecules of water absorbed on the electrode but in the opposite direction. The first stage of the process is a slow one and it can be represented by the following diagram:

$$\underset{\text{(solution)}}{H_2O} + \underset{\text{(electrode)}}{H-O\,|\,\overset{\oplus}{M}} \longrightarrow \underset{\text{(solution)}}{H_3O^+} + \underset{\text{(electrode)}}{OH^-\,|\,\overset{\oplus}{M}}$$

It will be seen that hydroxonium ions are formed in the solution and hydroxyl ions at the electrode. This slow process is followed by three processes taking place in quick succession during which the hydroxyl ions first discharge (the ⊕ symbol designates a positive charge, i. e. lack of electrons at the anode), then combine under liberation of atomic oxygen that in its turn gives molecular oxygen:

$$\begin{aligned} OH^-\,|\,\overset{\oplus}{M} &\longrightarrow OH\,|\,M \\ 2OH &\longrightarrow H_2O + O \\ 2O &\longrightarrow O_2. \end{aligned}$$

Metals characterized by strong bonds of *M*—H type make the transfer of a

proton into the solution more difficult; such metals may be expected to cause high overvoltage on oxygen deposition, i. e. to behave quite contrary to how they would behave at the cathode during the discharge of hydrogen ions. In accordance with this theoretical assumption, platinum, palladium and gold are characterized by a low hydrogen overvoltage but a high oxygen overvoltage; in other cases an exact analogy does not exist because of the formation of oxides on the surface of the anode or by other secondary processes by which the deposition of oxygen is complicated.

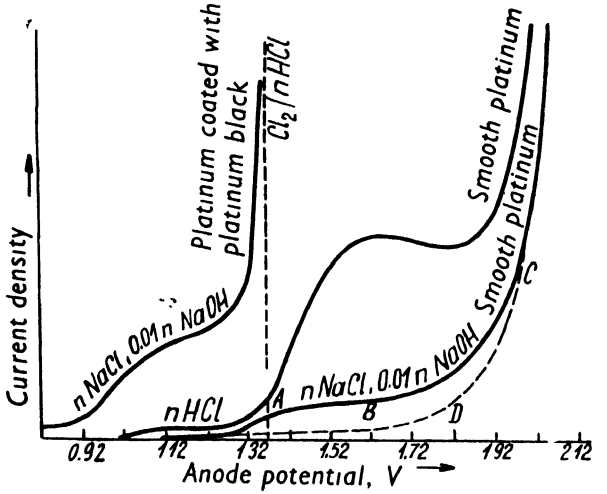


Fig. 26. Polarization on evolution of chlorine

c) *Halogen overvoltage*

If chlorine is to be evolved at the anode it is necessary to use insoluble platinum or irridium electrodes as other metals are anodically dissolved in chloride solutions. From among nonmetallic substance, graphite or magnetite suit the purpose. When electrolyzing a normal solution of sodium chloride at a platinum electrode coated with platinum black after adding a small quantity of 0.01 N-sodium hydroxide to ensure a definable alkalinity a weak current begins to pass through the electrolyzer slightly before the corresponding equilibrium potential of the chlorine electrode is reached. This is caused by depolarization of the anode which in its turn is due to the fact that the chlorine liberated from the electrolyte at less than atmospheric pressure does not exclusively remain within the electrode but partly dissolves itself in the solution. This weak current is consumed for replacing such losses on chlorine. With increasing voltage the current rises slowly at first and then, before the attainment of the equilibrium chlorine potential, rapidly, however, without exceeding the same. Thus chlorine will be evolved at platinized platinum without

overvoltage (see Fig. 26) even at fairly high current densities. The same holds good for bromine and iodine.

An electrode of smooth platinum behaves quite differently: although at low current densities chlorine is evolved without overvoltage as in the previous case, at higher current densities or after the electrolysis has been going on for a certain time the potential suddenly rises by some 0.6 V above its equilibrium value so that any further liberation of chlorine is already associated with high overvoltage. At this stage a characteristic deformation can be seen on the current curve corresponding to a normal solution of sodium chloride which is still more obvious if a normal solution of hydrochloric acid is used. The current density increases slightly at first until it about reaches the equilibrium chlorine potential. From that point on its rise is steeper but ceases completely soon after; the curve then runs parallel to the potential axis, i. e. in a similar manner as observed in the case of the limiting current. In this case, however, limiting current is not involved as its magnitude would change on stirring the solution. On increasing the current density still further, the curve assumes the usual logarithmic shape and approaches the potential values valid for the electrolysis of the alkaline solution of sodium chloride at smooth platinum. Polarization which takes place most readily in the case of chlorides, more reluctantly in the case of bromides, and is comparatively most difficult in the case of iodides, is more important the lower the concentration of the halide used, the higher the current density and the more alkaline the solution. At the same time it may be observed that the gas evolved at higher potentials contains a certain amount of oxygen.

The above-mentioned rise of the anode potential on evolution of chlorine at a smooth platinum electrode was previously ascribed to insufficient velocity of combination of atomic chlorine to form chlorine molecules: this process was considered to be retarded by a simultaneous deposition of a small quantity of oxygen on the surface of the anode. This explanation seemed probable at first sight because at the reversible potential of chlorine in a normal solution (π = = 1.36 V) hydroxyl ions can actually discharge to a certain degree (oxygen evolution from neutral solution at a smooth platinum electrode begins at 1.27 V). The more alkaline the solution is, the lower potential for the discharge of the hydroxyl ions and, consequently, the lower current densities are needed to induce the polarization of the halogen ion.

This theory also agrees with the fact that no polarization can be observed on electrolysis of bromides in an acid medium because in such a solution bromine is liberated prior (at 1.06 V) to oxygen (at 1.68 V). If the solution is, however, alkaline so that the hydroxyl ions start to discharge already at 0.86 V, the polarization of bromine manifests itself quite clearly. On electrolyzing iodine the deposition potential of which equals 0.535 V, no polarization at all can be observed either in acid or neutral solution in accordance with our previous explanation. In the case of an alkaline solution only a slight trend towards polarization can be observed.

Until now the above-mentioned theory explained all phenomena associated with polarization on halogen liberation. One phenomenon has not been explained; in the presence of substances accelerating decomposition of hydrogen peroxide (such as $MnCl_2$, $FeCl_2$, finely dispersed silver or animal charcoal) the electrode will be polarized much sooner. The recent hypothesis is free from this drawback: according to it the reversible evolution of chlorine is accompanied by an irreversible formation of hydrogen peroxide due to the combination of discharged hydroxyl ions. Hydrogen peroxide may in turn either oxidize halogen ions to elements or decompose itself with an ensuing formation of oxygen. As oxygen accumulated at an electrode determines its potential, it follows that substances decomposing peroxide accelerate the polarization of the anode in the same way as an increased alkalinity and temperature of the solution does. As the readiness of halogen ions to be oxidized by hydrogen peroxide increases respectively in accordance with the sequence chlorine, bromine, iodine, there will be least accumulation of oxygen in a iodine electrode, which, therefore, is subject to practically no polarization.

3. Cathodic deposition of metals

Most metals commence to be deposited from solutions of their own salt in the course of cathodic polarization near their reversible potentials so that at sufficiently low current densities these processes can be considered to be practically reversible (see Fig. 27.). At higher current densities the cathode

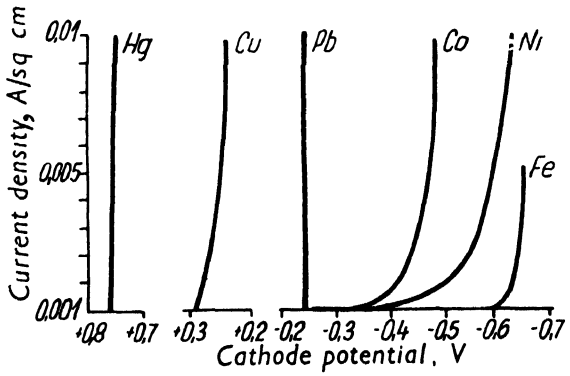


Fig. 27. Deposition potentials of certain metals at different current densities

potential assumes a somewhat more negative value partly as a result of concentration polarization and partly on account of the slowness of some phase of cathodic process which commences by the transfer of an ion onto the electrode, continues by its discharge and ends by a final orientation and incorporation

of the atom into the crystal lattice of the metal. It seems that among these steps the growth of crystals from their nuclei is the slowest one.

Contrary to most metals, iron, cobalt, and nickel are deposited at the cathode even at very low current densities at a potential that is by 0.2 to 0.3 V more negative than the reversible potential. The least comparative irreversibility on deposition is manifested by iron, the greatest by nickel. Polarization decreases as temperature is raised so that at temperatures exceeding 70 °C iron will be deposited in a reversible way whilst deposition of nickel and cobalt are associated with an overvoltage of about 0.05 V even at 100 °C. It seems that a higher temperature accelerates the conversion of the unstable form in which metals are initially deposited to a stable one.

A rather high degree of polarization is sometimes encountered on deposition of metals from solutions of their complex salts (for example silver from a cyanide solution).

The deposition of metals may be accompanied by the discharge of hydrogen ions which are present in every aqueous solution. Taking into account the respective equilibrium potentials and possible polarization phenomena as well it is possible to determine beforehand whether at a given temperature and concentration the deposition of metal or the discharge of hydrogen ions will have priority. In the same manner it can be determined in what sequence the individual metallic ions will be deposited from a solution containing two different salts or more.

Should there be no interaction of the deposited metals (i. e. should no alloy be formed), a simultaneous deposition of different metals is possible only when their deposition potentials are equal. As these deposition potentials are determined by the sum of reversible (reduction) potentials and of the corresponding overvoltage value ω, the condition of a simultaneous discharge of cations A^+ and B^+ (one of which may be the hydrogen ion) can be written in the following form:

$$\pi_A - \omega_A = \pi_B - \omega_B.$$

The numerical value of ω will be subtracted here, as cathodic deposition potentials bear a negative sign. If Nernst's law is used to express the value of the reversible potential the equation assumes the following form:

$$\pi_A^\circ + \frac{RT}{nF} \ln a_A - \omega_A = \pi_A^\circ + \frac{RT}{nF} \ln a_B - \omega_B. \qquad \text{(VII-23)}$$

As long as the current density used is below the value at which the potential corresponds to the deposition of B and the conditions for the equation (VII-23) are not fullfilled, the more noble metal A will be deposited alone. If this value of the current density is exceeded both cations discharge simultaneously.

The ratio in which both ions are deposited on further increase of the current density depends on relative position and shape of the current curves. It will

be seen from Fig. 28 that the current curves may run almost parallel (I) or take divergent courses at higher current densities (II), or be convergent at first, then cross each other and diverge in the end (III). In all these cases the more noble metal will be deposited at the cathode potential π at a rate directly proportional to the length of the ordinate d_1 while the less noble metal B (or hydrogen) will be deposited at a rate directly proportional to the length of d_2. From the total current a part determined by the quotient $d_1/(d_1 + d_2)$ will be used up in discharging the ion A^+ and a part determined by the quotient $d_2/(d_1 + d_2)$ in discharging the ion B^+; the mixtures thus de-

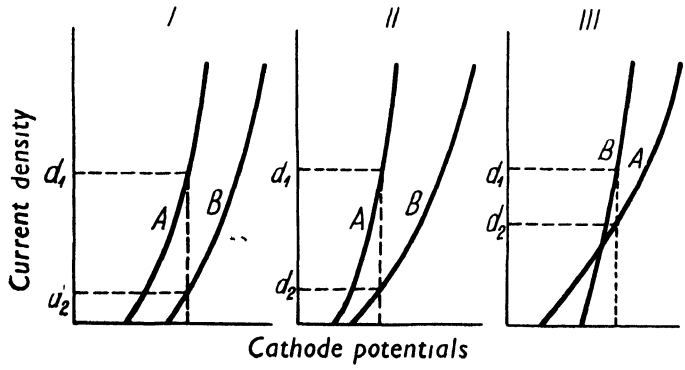


Fig. 28. Deposition potentials of two cations at various current densities

posited at the cathode (an alloy for instance) will contain both elements, A and B, in the ratio of the equivalents d_1/d_2 .In case of curve I (Fig. 28) the difference $(d_1—d_2)$ is nearly constant and the ratio d_1/d_2 diminishes at higher current densities. In case II the composition of the deposit does not change at various current densities as the ratio of d_1/d_2 remains constant. If both curves intersect (III) then at the potential corresponding to the point of intersection $d_1 = d_2$ both products of cathodic reduction, A and B, are deposited in proportion of their respective equivalents, i. e. 1 : 1. Below this point element A will predominate in the deposited mixture while above this point element B will be in excess.

In order to get a clearer picture of conditions existing on deposition of metals, let us discuss some examples. The deposition potential of silver from a normal solution of its salt almost equals the standard reduction potential $\pi^{\circ}_{Ag} = +0.8$ V, and the potential of hydrogen evolved from a neutral solution π_{H_2} equals $0.059 \log 10^{-7} = -0.41$ V. Both potentials are so wide apart that not even the polarization occurring at higher current densities can considerably affect the relative position of both curves. For this reason, silver will be deposited from the solution prior to hydrogen until practically all Ag^+ ions will be

eliminated; sufficient separation of respective potentials makes it even possible to carry out electrolysis in an acid solution without any risk of simultaneous hydrogen deposition.

In cases where the difference in the standard potential is not so great, both curves can be made to run closer or farther apart by a suitable choice of reaction conditions; thus the simultaneous deposition of both cations can be either facilitated or made more difficult. It is possible, for example, to carry out a simultaneous cathodic deposition of tin and lead from the solution of their chlorides; it only requires a suitable adjustment of respective concentrations of their salts in the solution because the standard potentials of both these metals are very near to each other ($\pi^{\circ}_{Sn} = -0.14$, $\pi^{\circ}_{Pb} = -0.13$). If an acid solution is used hydrogen ions should be discharged theoretically prior to both metals ($\pi^{\circ}_{H_2} = 0$), yet in fact, the hydrogen overvoltage at both metals is so high that no hydrogen will be evolved at all.

Analogously to this case the existence of hydrogen overvoltage makes it possible to produce a number of less noble metals by an electrochemical process. The standard potential of cadmium $\pi^{\circ}_{Cd} = 0.40$ is very close to the reversible potential of hydrogen in a neutral solution, $\pi^{\circ}_{H_2} = -0.41$ V; it could be expected that in such a medium both cations will be discharged simultaneously, while in an acid solution only hydrogen will be evolved. Because of a high hydrogen overvoltage at cadmium, attaining about 1 V already at a current density of 1 mA/sq.cm, no hydrogen will be evolved whilst only cadmium will be reduced as its deposition potential is much more positive than the actual deposition potential of hydrogen. In the same way electrolytical deposition of other base metals, such as zinc, iron, nickel, tin and lead from their aqueous solutions can be explained. Without this hydrogen overvoltage the deposition of some of these metals from a neutral medium would be associated with substantial liberation of hydrogen while for instance in the case of zinc, hydrogen would be even the only product of the electrolysis at the cathode.

The distance between the current curves of two metals may sometimes be controlled by temperature as the value of the overvoltage varies under its effect. The deposition potentials of nickel and zinc on electrolysis of their salts in aqueous ammonia solution at 20 °C differ only slightly because the high overvoltage for nickel reduces the difference between the respective reversible potentials, thus making simultaneous deposition of both metals quite possible. On the other hand overvoltage for nickel at 90 °C is considerably lower so that the difference between the deposition potentials increases and simultaneous deposition of nickel and zinc is no longer possible.

Another method of control of the mutual position of the current curves is based on changes of concentrations of ions in the solution. Since a mere dilution would result in a greatly increased resistance of the electrolyte and the reserve necessary for replacement of deposited ions would be reduced, the required lowering of concentration can be attained in a more advantageous manner by converting simple ions to complex ones with a low degree of dis-

sociation. For example, the current curve related to deposition of copper from solution of copper sulphate and the corresponding current curve related to hydrogen evolution are at normal current densities so far apart that copper is the only product of electrolysis at the cathode. If, however, the potential of copper deposition is lowered by converting the cupric ions to the very stable complex $Cu(CN)_2^-$ which has a low degree of dissociation, the current curve of the copper will be shifted towards considerably more negative potentials; in such a case hydrogen and copper will be deposited simultaneously; should there be an excess of the alkali cyanide, the deposition of copper would cease altogether.

Simultaneous deposition of copper and hydrogen can also occur on electrolyzing a sufficiently diluted solution of copper sulphate at very high current densities. In this way the current curve representing the deposition of copper will reach the region of the limiting current and the potential will assume so much negative value that even hydrogen ions will commence to be discharged.

Another example of the effect of a change of concentration upon the cathodic process can be found in electrolysis of a solution of salts of copper and bismuth. As the respective deposition potentials, which practically equal the equilibrium potentials are fairly close ($\pi^{\circ}_{Cu} = 0.34$ V, $\pi^{\circ}_{Bi} = 0.23$ V) the two metals cannot be separated from each other electrolytically. On the addition of cyanide, however, Cu^{++} ions are converted into cupricyanide ions from which copper cannot be deposited prior the cathode reaches the potential π_{Cu} equalling to about -1.0 V. As bismuth does not form cyanide complexes the resulting difference in potentials, $\pi_{Bi} - \pi_{Cu} = 1.23$ V is a sufficient guarantee that during electrolysis only bismuth will be preferentially deposited.

In other cases the change of cation concentration is used to bring both deposition potentials nearer and to have both metals deposited at the same time as an alloy. Copper and zinc are deposited separately from a common sulphate solution as their respective deposition potentials which practically equal the equilibrium potentials are far apart ($\pi^{\circ}_{Cu} - \pi^{\circ}_{Zn} = 1.1$ V). On converting both cations into complex cyanide anions, i. e. $Cu(CN)_2^-$ and $Zn(CN)_4^{--}$, an alloy can be obtained — brass — of any desired composition provided suitable concentrations, temperatures and current densities have been used. The deposition of this alloy is made possible by bringing the current curves of both metals closer together; this in turn is brought about by the fact, that the deposition potential of copper in the cyanide solution deviates much more from its standard value (due to a great stability of the cuprocyanide complex) than the potential of zinc, the complex anion of which is dissociated into simple ions in a fairly high degree. The deposition of brass is also made easier by the fact that the alloy contains both metals in a solid solution. The formation of it is, therefore, accompanied by the decrease in free energy of the system and consequently by the decrease of the potential necessary for the discharge of zinc cations on copper; in other words there is a depolarizing action due to the formation of a solid solution.

The above-mentioned process of depolarization which in the previous case merely favoured the cathodic deposition of the alloy can be in the other cases the main factor that makes electrochemical reduction possible. In such cases depolarization is caused by the fact that the metal deposited from the solution can either be dissolved in the cathode material or form a compound with it; as partial molal free energy of the metal is lower in this state than it would be in the pure form, it can be deposited on the cathode at a less negative potential. A technically important example of such a process is the electrochemical preparation of sodium amalgam from a sodium chloride solution, using a mercury cathode. While the standard reduction potential of sodium ions on metallic sodium is $\pi^{\circ}_{Na} = -2.71$ V the reversible potential of sodium ions, being deposited from a solution of sodium chloride of an activity $a_{Na^+} = 1$ on sodium amalgam containing 0.2 p. c. Na, is $\pi_{Na\,Hg} = -1.867$ V. Apart from sodium, also hydrogen cations can be discharged from a neutral solution at a reversible potential $\pi_{H_2} = -0.41$ V. At the mercury cathode, however, the actual liberation of hydrogen does not commence prior the cathode attains a potential of about — 1.26 V because of high overvoltage When the electrolytic cell is under current, overvoltage increases still more; further increase of the hydrogen overvoltage is due to the fact that the solution in the proximity of the electrode manifests a slightly alkaline reaction because a small amount of sodium has been dissolved in it. As a result of all these effects hydrogen cannot be evolved on mercury in greater amounts but at a potential slightly above —2.0 V.

At such conditions sodium ions are preferentially discharged and a diluted amalgam is formed at which the reduction potential of sodium is lowered. In order to remove quite definitely the risk of hydrogen being evolved during preparation of amalgam a saturated solution of sodium chloride is electrolyzed and the formed amalgam removed before the sodium content exceeds about 0.2 p. c.; both these measures are taken to maintain the potential π_{NaHg} at the least possible negative value. The same holds good for the preparation of potassium amalgams.

The possibility of preparation of sodium or potassium amalgams by an electrochemical process is technically utilized for the production of alkali hydroxides by decomposition of amalgams with water.

4. Anodic dissolution of metals

In the course of electrolysis there may occur either discharge of anion at the anode, for instance,

$$2\,OH^- = H_2O + \tfrac{1}{2}\,O_2 + 2e$$
$$2\,Cl^- = Cl_2 + 2e$$
$$2\,SO_4^{--} = S_2O_8^{--} + 2e,$$

or the material of the electrode can be dissolved. It can be stated generally that the preferential process will be that one, which requires lowest potential and which proceeds at a highest rate.

Therefore, the electrode will be dissolved when its dissolution potential will be lower than the potentials corresponding to any possible oxidation reaction of the anions present in the solution. To initiate such a process of dissolution it is only necessary to raise the potential of the anode just slightly above the value of the reversible potential of the system. On ncreasing the current density, concentration polarization manifests itself to an ever increasing degree. This polarization is due to an accumulation of ions at the anode but it can be substantially suppressed by intensive stirring of the solution, or by raising the temperature. Polarization with some metals is too great to be explained by mere concentration changes. The cause may be some irreversible process occurring on anodic dissolution of the electrode.

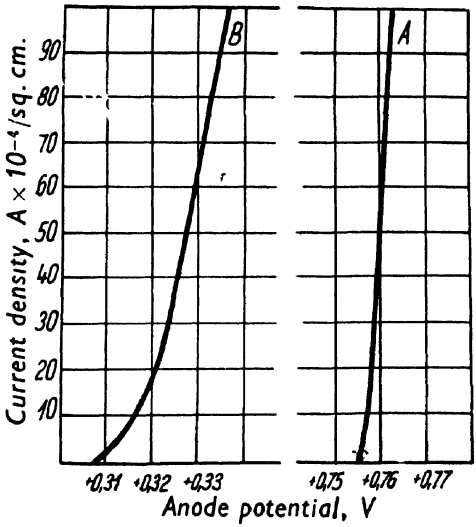


Fig. 29. Anode potentials of mercury and copper at various current densities

A typical example of dissolution of the anode being associated merely with concentration polarization is encountered in the case of mercury; the relation between anode potential and current density is graphically represented in Fig. 29. which illustrates the conditions prevailing in a 0.66 normal solution

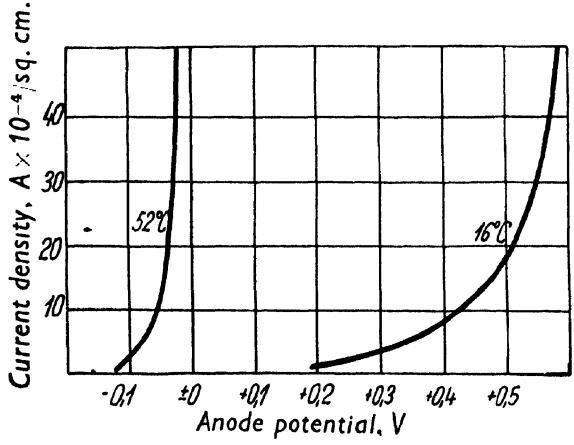


Fig. 30. Anode potential of nickel at various current densities at 16 °C and 52 °C.

of $Hg_2(NO_3)_2$ and of 0.1 normal solution of HNO_3 at 23 °C (curve *A*). The curve representing the anode current for copper in a solution of $1N$—$CuSO_4$ and $3N$—H_2SO_4 (curve *B*) deviates more from a vertical than would c rrespond to mere concentration polarization; the same holds good for anodes of zinc and cadmium. Still greater irreversibilities are manifested by anodes of iron, cobalt and nickel. It can be seen from Fig. 30 that nickel in a normal solution of $NiCl_2$ at 16 °C begins to dissolve at a much more positive potential than the reversible one ($\pi^{\circ}_{Ni} = 0.25$ V) and with increasing current densities the current curve is displaced towards considerably high values of anode potential. At higher temperatures the dissolution curve has a steeper course indicating a drop in polarization probably due to an increasing velocity of the slow stage of the dissolution process which is the cause of polarization

In the case of anodically poorly soluble metals (such as nickel) the structure of the material may be of some importance. Rolled or forged metals have greater dissolution pressure than cast ones. As the material is heterogeneous the mechanically treated parts are dissolved first while the soft ones are loosened from the anode and deposited at the bottom of the vessel in the form of slurry.

While some metals, such as zinc, enter the solution as ions of always the same valency, other metals (e. g. Cu, Hg, Sn, Pb, Cr, Au, Fe, Co, Ni, Tl) can form ions of different valencies in the anodic process. In order to solve the problem of ionization in stages *Luther's rule* is applied.

In the case of metal forming two cations, M^{z}_{1} and M^{z}_{2}, there will coexist the equilibria of three systems M/M^{z}_{1}, M/M^{z}_{2} and M^{z}_{1}/M^{z}_{2} with corresponding oxidation potentials ε^{0}_{2}, ε^{1}_{0}, $\varepsilon^{0}_{1,2}$ or reduction potentials π^{0}_{1}, π°_{2} and $\pi^{0}_{1,2}$. Let us assume that the ion M^{z}_{2} has a higher valency than M^{z}_{1} ($Z_2 > Z_1$). The standard free energies related to individual respective processes are thus:

$$M = M^{z}{}_{1}, + z_1 e; \; \Delta G^{0}_{1} = - z_1 F \, \varepsilon^{0}_{1} = z_1 F \, \pi^{0}_{1}.$$

$$M = M^{z}{}_{2}, + z_2 e; \; \Delta G^{0}_{2} = - z_2 F \, \varepsilon^{0}_{2} = z_2 F \, \pi^{0}_{2}.$$

$$M^{z}{}_{1} = M^{z}{}_{2} + (z_2 - z_1)\, e; \; \Delta G^{0}_{1,2} = - (z_2 - z_1) \, F \, \varepsilon^{0}_{1,2} = (z_2 - z_1) \, F \, \pi^{0}_{1,2}.$$

It follows from the thermodynamical laws that the change in free energy ΔG^{0}_{2} associated with the passage of metal atoms into the state of ions of higher valency equals the sum of the change in free energy ΔG^{0}_{1} corresponding to the pass age of the metal into the state of ions of lower valency and of the change $\Delta G^{0}_{1,2}$ which occurs on oxidation of the lower valency ion to the higher valency, thus:

$$\Delta G^{0}_{2} = \Delta G^{0}_{1} + \Delta G^{0}_{1,2}.$$

On substituting the above-mentioned relationships, which express the individual changes in free energy, into the last equation, we obtain:

$$z_2 \varepsilon^{0}_{2} - z_1 \, \varepsilon^{0}_{1} = (z_2 - z_1) \, \varepsilon^{0}_{1,2}$$

or

$$z_2 \pi^{0}_{2} - z_1 \, \pi^{0}_{1} = (z_2 - z_1) \, \pi^{0}_{1,2}. \qquad \text{(VII-24)}$$

It will be seen from this equation — first derived by *Luther* — that the values of the potentials are not independent of each other. If for instance the standard potentials of the systems Cu/Cu^{++} and Cu^{+}/Cu^{++} equal $\pi_2^0 = 0.34$ V and $\pi_{1,2}^0 = 0.16$ V respectively at 25 °C, the potential of the system Cu/Cu^{+} ($z_1 = 1$, $z_2 = 2$) can be determined as follows:

$$2 \cdot 0.34 - \pi_1^0 = 0.16$$
$$\pi_1^0 = 0.52 \text{ V}.$$

On dipping a metal M into a solution containing its ions $M_1^{z_1}$ and $M_2^{z_2}$ a reaction takes place until an equilibrium is reached in compliance with the following equation:

$$(z_2 - z_1)\, M + z_1 M^{z_2} \rightleftarrows z_2 M^{z_1}.$$

The value of the equilibrium constant $K = a_1^{z_2}/a_2^{z_1}$ can be calculated starting from the assumption that the potential of the metal M must be equal at the equilibrium state with regard to both ions $M_1^{z_1}$ and $M_2^{z_2}$:

$$\pi_1^0 + \frac{RT}{z_1 F} \ln a_1 = \pi_2^0 + \frac{RT}{z_2 F} \ln a_2,$$

hence:

$$\ln K = \ln \frac{a_1^{z_2}}{a_2^{z_1}} = (\pi_2^0 - \pi_1^0) \frac{z_1 z_2 F}{RT},$$

or at 25 °C:

$$\log K = (\pi_2^0 - \pi_1^0) \frac{z_1 z_2}{0{,}05915}. \qquad \text{(VII-25)}$$

In the case just considered, $\pi_1^0 = 0.52$ and $\pi_2^0 = 0.34$, thus the equilibrium constant of the reaction

$$Cu + Cu^{++} = 2\, Cu^{+},$$

at 25 °C will have the following value:

$$\log K = -\frac{0{,}18 \cdot 2}{0{,}05915} \quad \text{or} \quad K = \frac{a_{Cu^+}^2}{a_{Cu^{++}}} = 8{,}22 \cdot 10^{-7}.$$

It will be readily appreciated that at a state of equilibrium and in the presence of metallic copper there can be merely a negligible amount of Cu^{+} ions apart from Cu^{++} ions in the solution.

On anodic dissolution of metals, if it takes place at equilibrium potentials, ions of different valencies are also formed in the ratio expressed by the equilibrium constant. So, for instance, copper anode emits Cu^{++} and Cu^{+} ions into the solution in a ratio that, under the afore-men ioned assumption and at

equilibrium state, the composition of the solution formed in the vicinity of the electrode at 25 °C corresponds to the equation:

$$a^2_{Cu^+}/a_{Cu^{++}} = 8.22 \cdot 10^{-7}.$$

At higher current densities, however, the dissolution of copper is associated with polarization and as a result of this at a higher anode potential a comparatively great amount of Cu^+ ions enters the solution than would correspond to dissolution under equilibrium conditions. The resulting solution is thus oversaturated with Cu^+ ions with regard to the concentration of Cu^{++} ions present; it is unstable and decomposes according to the equation $2\,Cu^+ = Cu + Cu^{++}$ till the concentration of Cu^+ drops to the equilibrium value. During this reaction metallic copper is precipitated in the form of crystalline powder which falls to the bottom of the electrolytic cell as anode slime. The behavior of gold on electrolytic refining is much similar: it dissolves at the anode and enters the solution predominantly in the form of trivalent ions and to a lesser degree also as univalent ions. Due to polarization the ratio of the formed Au^+ and Au^{+++} ions is higher than would correspond to the state of equilibrium; thus the monovalent ions of gold in the solution cannot exist in such a high concentration and decompose in accordance with the equation $3\,Au^+ = Au^{+++} + 2\,Au$ whereby metallic gold is deposited from the electrolyte in the form of loose tiny crystals

Contrary to copper and gold (for which $\pi^0_1 > \pi^0_{1,2}$) the equilibrium in the case of ions of Hg, Sn, Pb, Cr, Fe, Co, Ni and Tl (for which $\pi^0_1 < \pi^0_{1,2}$) is remarkably favourable for ions of the lower valency Thus if the metal dips into a solution with a higher concentration of ions of higher valency than would correspond to the equilibrium constant, there occurs a reaction in the course of which these ions share their charges with the metal and ions of lower valency are formed until the equilibrium state is reached (for example. $2\,Fe^{+++} + Fe = 3\,Fe^{++}$). Also in the case of anodic dissolution the mentioned metals are transferred into the solution predominantly in the form of ions of lower valency.

The above-mentioned conditions of anodic dissolution can change completely if the concentration of one ion entering the solution is kept extremely low by the formation of a suitable stable complex. The potential of Cu/Cu^+ in a solution where Cu^+ ions are bonded in a cyanide complex is so negative — the concentration of the remaining free cuprous ions being negligible — that its value is even below that of the dissolution potential of Cu/Cu^{++}; as a result, copper is transferred into the solution predominantly in the form of cuprous (univalent) cations. Analogously in the case of concentrated hydrochloric acid or solutions of alkali chlorides used as electrolytes, copper dissolves predominantly in the form of univalent ions because slightly dissociated cuprous-chloride complexes are formed.

In anodic dissolution of mercury at 25 °C the following potentials may be considered:

$$Hg = \tfrac{1}{2}\,Hg_2^{++} + e; \quad \pi_1^0 = 0{,}7988$$
$$Hg = Hg^{++} + 2e; \quad \pi_2^0 = 0{,}8544$$
$$\tfrac{1}{2}\,Hg_2^{++} = Hg^{++} + e; \quad \pi_{1,2}^0 = 0{,}9100.$$

On substituting these values into the equation (VII-25) we obtain the following value for the equilibrium constant of the reaction:

$$Hg + Hg^{++} = Hg_2^{++},$$

$$\log K = \frac{0{,}0556 \,.\, 2}{0{,}05915} \text{ or } K = \frac{a_{Hg_2^{++}}}{a_{Hg^{++}}} = 76.$$

In anodic dissolution of mercury in a solution of nitric acid, where both mercurous and mercuric salts are asumed to be completely dissociated, both the formed ions enter the solution in the ratio of their respective activities $a_{Hg_2^{++}}/a_{Hg^{++}} = 76$. When alkali cyanide is used as electrolyte the bivalent ions formed on dissolution are predominantly consumed for the formation of the complex $Hg(CN)_4^{--}$. As a result of the formation of this complex the concentration of free Hg^{++} ions decreases considerably in accordance with the negligible degree of dissociation of the above-mentioned complex, and consequently the dissolution potential of the system Hg/Hg^{++} also decreases. For this reason, mercuric ions converted to mercuricyanide complex can be considered to be practically the sole product of the anodic process while the amount of univalent mercury ions is quite negligible. Contrary to this, on dissolving mercury in a solution of hydrochloric acid mercurous ions are predominantly formed due to the slight dissociation of mercurous chloride, the main product of the reaction.

A similar consideration can be applied to the cathodic processes. In a solution of mercuric nitrate bivalent mercury will be reduced to univalent until the ratio of the respective activity of the mercurous salt formed and the mercuric salt still remaining reaches the equilibrium value. During the course of further reaction the ratio of activities of both ions in the solution will not change any longer, and metallic mercury will be deposited. Therefrom, it is evident that mercuric nitrate cannot be quantitatively reduced to mercurous salt. Bivalent mercury can be reduced practically completely to univalent in the case of mercuric chloride. As the solubility of the mercurous chloride formed by the reduction and consequently also the concentration of Hg_2^{++} ion is very small the equilibrium between the ions in the solution will be attained only then, when nearly all Hg^{++} ions will be reduced to univalent ones. On the other hand on reduction of the very slightly dissociated cyanide complex $Hg(CN)_4^{--}$ the equilibrium between mercurous and mercuric ions is reached at the very beginning of electrolysis as soon as a hardly noticeable amount of Hg_2^{++} ions has been formed; from that moment on metallic mercury will be deposited at the cathode with practically 100 p. c. yield.

5. Passivity

Some metals (Fe, Cr, Ni, Co) are known to acquire chemical passivity on being exposed to the action of some oxidizing agent. So, for instance, iron which has been dipped into concentrated nitric acid dissolves only for a short time and then the dissolution suddenly ceases while the surface of the iron acquires a metallic brightness The metal made passive in this way can neither be dissolved in diluted acids nor does it displace the more noble metals from solutions of their salts. Iron which is passivated by strong oxidizing agents only returns to its normal state under the action of reducing agents or by being exposed to the action of humid atmosphere for a certain period. In the case of nickel and especially in the case of chromium a very slight oxidation by atmospheric oxygen is sufficient to induce an almost permanent passivity of these metals. This tendency towards spontaneous passivation manifested by chromium even in its alloys with iron is the reason for the excellent resistivity of stainless steel against corrosion.

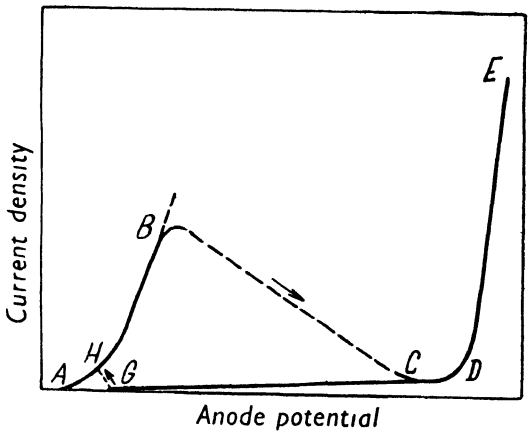


Fig. 31. Anodic passivity.

A similar phenomenon is encountered in the case of electrochemical or anodic passivation which occurs on anodic polarization of electrodes made of the above-mentioned metals. Apart from these, anodic passivity can be observed with vanadium, tungsten, molybdenum, gold, metals of the platinum group and — under particular conditions — also copper, tin and bismuth. The transition from the active to the passive state is displayed by the fact, that instead of the anodic process, most likely to occur from the thermodynamic point of view, another process takes place — without apparent causes — requiring a higher anodic potential. In the passive state of the metal other kinds of ions are emitted into the electrolyte, different from those in the active state, or alternately dissolution of the anode almost ceases altogether while oxygen or other gas is liberated at it instead. Passivity in the electrochemical conception represents the resistance which hinders the dissolution of metals on their transition to the state of ions during the anodic treatment.

If, for instance, nickel is polarized in a solution of sulphuric acid with gradually increased anodic potential, the metal first dissolves in the form of bivalent ions in exact agreement with *Faraday's law* (Fig. 31, curve *AB*). At a definite moment

the state corresponding to point B is reached after which the density of the current suddenly drops while the anode potential quickly increases (curve BC). This drop of the current density is due to the transition from the active state of nickel to a passive state which is associated with a marked drop in the rate of dissolution of the metal. On increasing the potential still further, the value of current density which reached its minimum value at point C has once more a rising tendency (curve CDE) due to increasing evolution of oxygen formed by the discharge of hydroxyl ions. Meanwhile the anode is still dissolved but only to a very slight degree. On decreasing the current density starting from point E, the active condition is not regained right at point C but only at point G where the potential changes with a jump to the value of point H on the initial AB curve. From this point on the dissolution of nickel recommences on increasing the anodic potential once more in the normal way along the AB curve.

The behavior of nickel on anodic polarization is matched by the behavior of iron and cobalt on the surface of which oxygen is also liberated at higher current densities. Chromium anode dissolves at low current densities to form bivalent cations. When it becomes passive its potential increases by about 1 Volt. With further increase of potential chromium enters a state called transpassive state in which instead of bivalent ions hexavalent ions are formed which react with the hydroxyl ions present in the electrolyte to form chromate ions according to equation:

$$Cr^{++++++} + 8\ OH^- = Cr\ 0_4^{--} + 4\ H_2O.$$

Since the potential necessary for the discharge of hydroxyl ions is still higher than that of the process $Cr \rightarrow CrO_4^{--}$ no oxygen is evolved at the anode and the chromium dissolves quantitatively giving chromate ions.

This tendency to passivity increases in the case of the four metals mentioned in the following order: Fe-Co-Ni-Cr. The transition of the metals from active to passive state is greatly influenced by the nature of anions in the electrolyte. The greatest effect is made in this respect by hydroxyl ions with ClO_3^-, CrO_4^{--}, NO_3^- and SO_4^{--} ions following in the indicated order which means that the onset of passivity can be reached at the rather low current density in alkaline solutions, while in an electrolyte containing sulphates much higher current density is required. Contrary to this, halogen ions sometimes inhibit the onset of passivity (for instance in the case of nickel and iron). Also higher temperatures and stirring of the electrolyte retard the attainment of passivity.

Passivity is an artificially induced state and the passivated metal regains its activity after some time, either spontaneously or after a suitable treatment. Passivity can be annulled, for instance, by restoring the initial state of the surface either through reducing agents or by removing the outer layer by emery paper. It can be equally achieved by touching the passivated metal with a piece of less noble metal (for instance zinc bar) in a solution of diluted acid

or by dipping the metal into a fused alkali chlorides. The most efficient means for annulation of the passive state is cathodic polarization using the passive metal as a cathode and allowing hydrogen to evolve at it.

It has been ascertained that chromium is the metal which can be rendered passive most readily among all the metalls mentioned up to now. The same holds good to an even greater degree for metals of the platinum group and gold, their passive state being so stable that they can be anodically dissolved only under exceptional conditions. For example, gold emits its cations only into hydrochloric acid at a very low current density; at higher densities, especially, at a lower temperature and insufficient acidity of the electrolyte, gold is passivated very quickly and chlorine is then evolved at the anode. It is even harder to annul platinum passivity than that of gold; because of this, it is used as insoluble material for anodes, especially in the case of oxygen-containing acids. In ammoniacal solutions, or in concentrated hydrochloric acid, platinum, however, suffers appreciable anodic attack.

Although up till now opinion about the reasons of passivity is divided, it is more than likely that the passive state of a metal surface is due to a dense but very thin and, therefore, invisible coat of metal oxide which is formed as an adherent film at the surface of the electrode. The formation of such a film, the existence of which has been proved experimentally, can be explained as follows: when the anode dissolves it emits ions into the electrolyte till the vicinity of the electrode becomes saturated with them; according to the existing concentration of hydrogen ions normal or basic salt is then gradually precipitated from the solution in the form of a rather thick visible layer covering the anode. On a gradual diminishing of the effective area of the electrode current density considerably increases with an ensuing rise of anode potential till hydroxyl ions can be discharged at the electrode; these discharged ions react with the metal of the anode so that oxide is formed. As soon as this new translucent film which adheres firmly to the anode covers the entire area of the latter, evolution of gaseous oxygen occurs because the oxide film is impermeable for metallic ions. The bubbles of evolved oxygen finally throw off the first visible thick layer of salt which then dissolves in the surrounding electrolyte whereby the surface of the passivated metal has once again the same appearance as it had in the active state. When the passivation process has ended the metal behaves like a more noble metal as it now has a film of metal oxide adhering to its surface and separating it mechanically from the electrolyte.

The existence of this thin film is indicated by certain phenomena such as lesser photo-electric emission or lesser reflection of polarized light by the passivated surface. compared with the corresponding properties of active metal surfaces. The resistance to acids of these surface oxides resembles the resistance of oxides formed on heating of metals in air.

The effect of the addition of chlorides to the electrolyte which sometimes hinders the passivity of metal is explained in the following manner: chloride ions can penetrate through some oxide films and make them more porous, i. e.,

more permeable for ions of the anode metal. The particular behavior of chrome is ascribed by some authors to its being coated with a film of chromium trioxide in its transpassive state, which is continually being dissolved in the electrolyte while the anode is oxidized repeatedly with the formation of a new film of chromium trioxide.

Sometimes the dissolution of the anode alm st ceases but, unlike the previous case,a permanent and visible layer of precipitate adheres to the anode; this phenomenon is called mechanical passivity the causes of which are in principle the same as those of chemical passivity.

Mechanical passivity occurs for example on the anodic polarization of lead in sulphuric acid solution. The lead first dissolves and forms bivalent ions that combine with sulphate ions to form a porous insoluble coat of lead sulphate on the anode. The effective current density at the remaining uncovered area of the anode then reaches such high values, that the anodic reaction $Pb \rightarrow$ $\rightarrow Pb^{++} + 2e$ cannot satisfy the requirements associated with the passage of the given current; therefore the potential of the anode rises to such a value that the lead anode commences to dissolve in the form of tetravalent ions according to the reaction: $Pb \rightarrow Pb^{++++} + 4e$ In a rather concentrated acid these ions pass into solution while in a more diluted acid hydrolysis occurs according to the reaction: $Pb^{++++} + 4\,OH^- = PbO_2 + 2\,H_2O$ with an ensuing formation of insoluble yet electrically conductive lead dioxide which deposits at the anode. The oxide layer is porous and, therefore, its thickness can increase till it becomes visible. The dissolution of the anode continues to some extent even after this but the major part of the current is consumed for the discharge of hydroxyl ions connected with the liberation of oxygen at the outer side of the oxide layer Should the electrolyte contain nitrates or chlorates in sufficient quantity lead sulphate no longer adheres to the anode and the metal is dissolved without hindrance forming bivalent ions.

Apart from this type of mechanical passivity at which current can pass across the conductive oxide layer at the anode even at a comparatively low anode potential under simultaneous evolution of oxygen, cases are also known in which the layer formed has a very poor conductance so that a much higher voltage is necessary for the passage of current. Such anodic behavior is manifested by aluminium or tantalum in suitable solutions if their thin, spontaneously formed non-conducting oxide layers have been thickened by anodic polarization in the so called "forming" process so that they separate the electrode from the electrolyte as a dielectric and prevent the passage of current at lower voltage. Only breakdown voltage which exceeds 10 V (sometimes 100 to 1000 V are necessary) can break through the insulating layer. Spark discharge appears, which is similar to the break-down of a condenser. If, however, such an electrode is connected as a cathode the current may flow at substantially lower voltages with simultaneous evolution of hydrogen. Aluminium or tantalum electrodes only let the current through in one direction, namely from the electrolyte towards the electrode, not in the opposite direction, they there-

ore act as valves. This property is utilized in engineering practice for the rectification of alternating current.

The electrolytic aluminium rectifier includes an aluminium electrode and another electrode of carbon, iron or lead. Both electrodes are suspended so that they face one another and are immersed in a solution of alkali borates, phosphates or carbonates. In a tantalum rectifier a solution of potassium carbonate, ammonium carbonate or sulphuric acid is used the other electrode being made of lead. The maximum voltage of the alternating current to be rectified must of course be lower than the breakdown voltage of the rectifier. When the rectifier cell is working, hydrogen is evolved at the tantalum or aluminium electrode while at the lead electrode oxygen is liberated.

In order to make use of both positive and negative waves of the alternating current the commercial rectifier comprises four individual cells interconnected according to the diagram indicated in Fig. 32

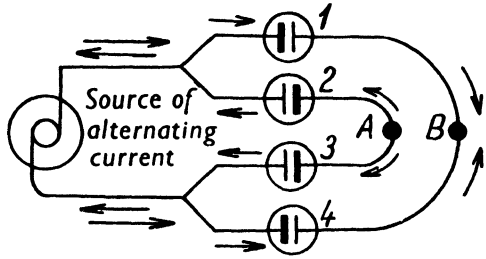


Fig. 32. Schematic drawing of an electrolytic rectifier.

The arrows indicate the direction of the flow of electrons, thick short lines represent the aluminium or tantalum electrodes which allow the current to pass only when they act as cathodes. It will be seen from the diagram that cells *1* and *4* let electrons through from left to right, cells *2* and *3* act in the opposite way; the electrones, therefore, always flow towards *B* and are taken from *A* which means that between these points, to which the electrical appliance is connected, there is a difference in D. C. voltage. Current rectification by means of this apparatus is not perfect; its efficiency amounts to some 60—70 per cent and with time it decreases still more.

E. ELECTROLYTIC REDUCTION AND OXIDATION

The deposition of metals or hydrogen at the cathode or the discharge of anions or dissolution of the anode are not the sole processes which may occur at the electrodes in course of electrolysis. If substances are present in solutions which can accept or release electrons at lower potentials than required by the aforementioned processes these substances are reduced or oxidized with priority. Such substances are generally called depolarizers

1 Electrolytic reduction

The reduction of a depolarizer at the cathode can be reversible or irreversible. A characteristical feature of all reversible processes is the fact that at reason-

ably low current densities the reduction of the depolarizer occurs at a quite definite and reproducible potential of the electrode which depends merely on the composition of the solution and may be associated with a hardly noticeable concentration polarization; it is only at higher current density at the electrode that a stronger polarization sets in due to irreversibility of some phase of the electrode process. Ferric ions are an example of a reversible depolarizer. They can inhibit the evolution of hydrogen at the cathode while being reduced themselves to ferrous ions. As no gas is liberated in this reaction it is assumed that the mechanism of depolarization consists in a direct transfer of electrons between the electrode and the ions:

$$Fe^{+++} + e = Fe^{++}.$$

Therefore, on increasing the terminal voltage of an electrolytic cell with two platinum electrodes dipping into an acidified solution of ferrous and ferric salt, both of them having the same molar concentration, the Fe^{+++} ions start being reduced as soon as the cathode potential is slightly more negative than the equilibrium potential of the redox system ($\pi^\circ = 0.77$ V). As long as the density of the current passing through the electrode is low, polarization is negligible. At higher current densities, however, the potential becomes more negative as the diffusion cannot compensate the quick depletion of Fe^{+++} ions occurring near the cathode. This concentration polarization which is the more marked the more the solution is diluted can be partly suppressed by stirring or by raising the temperature. If the current density has reached its limit value the potential steeply rises till it attains a value at which hydrogen or other cations can be deposited from the solution at the same time.

Sometimes the value of the redox potential attains even at low current densities such values that another simultaneous process is possible. For instance the cathodic reversible potential of the Ti^{++++}/Ti^{+++} system with the same concentration of both kinds of ions is about $\pi^\circ = 0.04$ V; if platinized platinum in a solution of sulphuric acid is used as a cathode the evolution of hydrogen commences at a potential also near zero and the current efficiency with respect to the reduction of Ti^{++++} ions will be comparatively low. Much better results can be achieved by replacing the platinum by another material, such as lead or graphite which have an appreciable hydrogen overvoltage, whereby the deposition potential of hydrogen becomes more negative as compared with the potential of the Ti^{++++}/Ti^{+++} system.

Some redox systems which appear reversible in the absence of current manifest a considerable polarization on the passage of current through the electrode in the course of electrolytic reduction. Reduction of pentavalent vanadium ions at a smooth platinum electrode in a solution of vanadic acid in sulphuric acid can be quoted as an example. This reduction takes place in two steps, i. e. $V^{V} \rightarrow V^{IV}$ and $V^{IV} \rightarrow V^{III}$. Similar behavior is manifested by molybdenic acid dissolved either in hydrochloric or sulphuric acid in the course

of reduction at a smooth platinum electrode. This reduction also occurs in two steps, namely $Mo^{VI} \rightarrow Mo^{V}$ and $Mo^{V} \rightarrow Mo^{III}$. Polarization is ascribed to the presence of an oxide film at the cathode which partly covers its surface; therefore, the effective current density at the uncovered surface area increases, as well as the cathode potential.

The depolarizers which are reduced irreversibly at the electrodes have no definable electrode potential. The mechanism of reaction of such substances is not very well known at present. According to one conception these reductions are assumed to be secondary reactions between depolarizer and the primarily deposited hydrogen at pressures below 1 atm. As for the evolution of hydrogen at such a low pressure a less negative potential, i. e. less energy is required, the reduction of the depolarizers occurs even before the normal deposition potential of hydrogen is attained.

The irreversible course of reduction processes occurs mainly in the case of unionized organic compounds and some inorganic ones, e. g. on reduction of nitric acid to hydroxylamine and ammonia. The reaction yield is affected by the potential of the electrode, its nature and state, concentration of the depolarizer, temperature and presence of a catalyst.

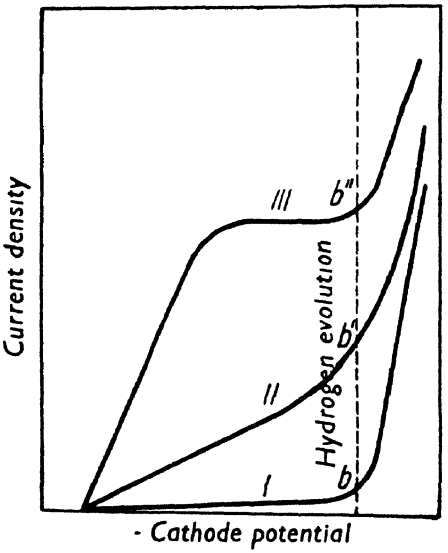


Fig. 33. Cathode potentials on electrolytic reduction.

The influence of the potential upon the yield at an irreversible course of cathodic reduction can be clearly seen in Fig. 33. In absence of a depolarizer the curve I represents the dependence of the current upon the cathode potential. The weak current flowing through the electrode between potentials *a* and *b* is caused by the diffusion of the hydrogen into the solution from the cathode. As soon as the potential attains the value *b* whereupon the pressure of the liberated hydrogen attains 1 atm the first bubbles appear. On increasing the potential still further the curve assumes a steep upward course. The presence of a depolarizer in the solution causes reduction prior to hydrogen evolution and the current density quickly increases from point *a* onwards. In the event of a comparatively slow depolarization reaction the dependence of the potential upon the current density is represented by curve *II*. The current efficiency with respect to reduction of the depolarizer is 100 per cent between points *a* and *b'* but it

decreases beyond point b' as in that region the reduction of the depolarizer is already associated with the simultaneous deposition of gaseous hydrogen. Curve *III* is a graphical representation of conditions under which the depolarization reaction proceeds very rapidly; in this case the potential increases slowly on the whole till the current density attains the value of the limiting current; from then on the potential curve runs parallel to the axis of abscissae up to the point b'', beyond which the current density increases once again, as under these conditions hydrogen ions discharge, too.

The relative position of the curves representing the evolution of hydrogen and the reduction of depolarizer respectively leads us to the conclusion that the greater the velocity of the depolarization process the better the results obtained i. e. a smaller part of the current is wasted on the deposition of hydrogen. As high current densities not only raise the cathode potential up to values close to the deposition potential of hydrogen but also rapidly decrease the concentration of the depolarizer in the vicinity of the electrode, the consumption of current is less, i. e. the current efficiency increases with decreasing current density. The current efficiency is raised by using cathodes with a large surface area and by the greatest possible concentration of depolarizer as well as by an efficient stirring of the electrolyte.

If the reduction process is represented by curve *II* it is possible to set a definite potential and to maintain it approximately at the desired level by changing the current density. Apart from this the cathode potential can be influenced by temperature and a suitable selection of materials for the electrodes. In so far as the material of the cathode has no catalytic influence upon the course of the reaction it can be said that the value of the cathode potential is a measure of its reducing power; i. e. the higher the cathode potential the more efficient the reduction of the depolarizer. On electrolytical reduction of nitrobenzene — for example — in an alkaline alcoholic solution using a platinum cathode at a current density of 0.001 A/sq. cm and a cathode potential π — — 0.6 V azoxybenzene is the main product. On raising the current density to 0.0035 A/sq. cm and the potential to $\pi = -1.0$ V then hydrazobenzene apart from hydrogen will be predominantly formed which represents a higher stage of reduction than azoxybenzene.

Electrodes of metals displaying a high hydrogen overvoltage, such as zinc, lead or mercury, make it possible to accomplish reduction of such substances which otherwise can be electrochemically reduced only with greatest difficulty. On carrying through the electrolysis, care must also be taken to keep the material of the electrode free from any impurities characterized by a low hydrogen overvoltage and to avoid the presence of salts of metals with a low hydrogen overvoltage in the solution; these metals can deposit at the cathode and completely prevent the onset of the reductions required. For example, on reducing nitrobenzene while using an electrode of zinc, lead, tin or mercury a good yield of aniline is obtained; if cathodes of material with a low hydrogen overvoltage are used (such as platinum or nickel) reduction ceases with formation of inter-

mediate products of reduction such as phenylhydroxylamine, azobenzene and hydrazobenzene (according to the nature of the medium).

Although it is certain, that cathodes with higher hydrogen overvoltage make it possible to attain a higher cathode potential without the liberation of gaseous hydrogen and hence a greater degree of reduction, the cause of this better efficiency when using such cathodes, is not known. As long as Tafel's theory was accepted according to which hydrogen overvoltage was due to a slow combination of atomic hydrogen to molecules, the reducing properties of cathodes with a high hydrogen overvoltage were ascribed to a greater accumulation of atomic hydrogen in the electrode. One of the recent theories states however, that metals with a high hydrogen overvoltage are characterized by weak bonds of the *M*-H type, from which hydrogen is more easily liberated and thus able to react with the depolarizer more rapidly than would be the case with strong bonds.

Though overvoltage at the cathode has a great influence upon the course of electrolytic reduction its magnitude does not always prove to be the decisive factor. Copper with spongy surface, for instance, makes it possible to reduce nitric acid to ammonia with a high yield although the overvoltage is comparatively low. On the other hand, when lead or zinc are used for the above-mentioned reduction, both showing a much higher hydrogen overvoltage, only the hydroxylamine stage is reached and only a limited quantity of ammonia obtained. In this case the catalytic effect of the material of the cathode apparently predominates while the importance of overvoltage is only secondary.

The state of the electrode surface has also some effect. A spongy surface sometimes decreases the required hydrogen overvoltage whereupon the current efficiency also becomes lower. In other cases a larger electrode surface allows for better contact between the active hydrogen and the depolarizer and so the rate of reaction between them is increased. Therefore, the reduction at platinized platinum electrodes sometimes results in high current efficiency, though the overvoltage is negligible.

The depolarizer concentration has no effect whatsoever on the nature of the reduction process but it could influence the current efficiency. This is so because with higher concentration the number of depolarizer ions in the vicinity of the electrode is reduced more slowly and the beginning of the hydrogen evolution at the cathode is delayed. Since with an increased depolarizer concentration the rate of electrochemical reduction at the cathode is increasing, the current density may even be raised without the possibility of hydrogen evolution.

Increase of temperature results in lowering the overvoltage and increasing the rate of the reduction of the depolarizer and the velocity of its diffusion to the cathode. The final effect of the increase of temperature is determined by that of the induced factors which prevails. In a process taking place under a comparatively low hydrogen overvoltage the yields are greater at higher temperature because reduction proceeds more quickly and the depolarizer diffusion to the electrode is intensified. Where reduction requires the application

of materials with high overvoltage the increased temperature is accompanied by an efficiency drop which is proportional to the decreasing overvoltage. This is caused by the favourable effect of the higher temperature on the rate of the reaction which is offset by the negative effect of the decreasing hydrogen overvoltage.

The addition of some substances to the solution will sometimes increase the rate of the reduction process and thus the current efficiency. Two types of such substances are known; the first type is represented by the salts of metals with a high hydrogen overvoltage which deposit at the electrode in the course of electrolysis, thereby increasing the electrode overvoltage. The second type of substances are salts of metals which are capable of existing in two oxidation stages (Ti, V, Cr, Fe and Ce). The effect od these catalysts is explained by, e. g. Ti^{++++} being reduced at the cathode more quickly than the depolarizer proper; the formed Ti^{+++} ions being a powerfull reducing agent will then react with the depolarizer, and in so doing again become oxidized into T^{++++} ions; the process will then be again repeated. For the described increase in the rate of reduction of the depolarizer only a small amount of the catalyst will be required since the individual reduction and oxidation cycles quickly alternate.

In electrochemical reductions the products formed at the cathode can diffuse to the anode, where they are reoxidized again. To prevent this phenomenon, the solution round the anode, called the anolyte, and the solution round the cathode, called the catholyte, are separated by a diaphragm.

To achieve the same effect, it is sometimes recommended to increase the current density at the anode. By this a potential is obtained at which, in addition to an undesirable reoxidation process, also the oxidation of other ions, oxidizable with greater difficulty (e. g. hydroxyl ions to oxygen) can take place. At a sufficiently high current density only a small part of the applied current will be consumed for the reoxidation process, whereas, the major part will be appropriated for the oxygen formation. The discharge of hydroxyl ions can be further promoted, i. e. it can be made possible already at low current density, if for the anodes we use materials with low oxygen overvoltage, e. g. iron or nickel in alkaline solutions.

Electrochemical reductions in inorganic industry are limited to the large scale manufacture of alkali metal amalgams from which hydroxides, sodium sulphide, hydrosulphite etc. are produced. On the other hand in small scale production electrochemical reductions are frequently applied to the preparation of compounds which are difficult to prepare in a chemical way (metal salts with lower valence, e. g. Ti, Mo, V, U and Cr).

2. Electrolytic oxidation

As long as depolarizer oxidation at the anode proceeds in a reversible manner the process can be explained as simply as at cathodic reversible reduction. Thus e. g. the oxidation of the ion Fe^{++} begins to proceed at an exactly reproducible

anodic potential only slightly more positive than the respective equilibrium redox potential. During the passage of a higher current through the anode the potential will rise slightly as a result of concentration polarization caused by the slow diffusion of the ions Fe^{++} from the solution to the anode and of the ions Fe^{+++} in the opposite direction. When finally the current density is so high that the oxidation rate is higher than the diffusion rate, still other oxidation processes start at the electrode, e. g. the discharge of chloride ions forming chlorine, evolution of oxygen or the dissolution of the electrode material.

In a similar way in which the oxidation of the bivalent iron cations to the trivalent is explained by the direct transfer of electrons from the solution to the electrode, also the oxidation of some anions can be explained by this simple reaction mechanism, e. g.

$$MnO_4^{--} = MnO_4^{-} + e,$$

$$Fe\,(CN)_6^{----} = Fe\,(CN)_6^{---} + e.$$

Irreversible anodic processes are still less understood than the reduction processes at the cathode, because in addition to irreversible oxygen evolution they are further complicated by the passivity phenomena at the electrode. From the analogy with the irreversible reductions at the cathode it has been concluded that in this case also proceeds a secondary reaction in the course of which the primarily evolved oxygen may already oxidize the depolarizer at a pressure of less than 1 atm. It has been also proved by experiment that sometimes the same factors influencing the electrolytic reduction have a similar effect upon irreversible oxidation processes at the anode. Hence e. g. the oxidation power of a platinum electrode, with which it is possible to work in a limited range with graded potentials, will be proportionally higher with a higher applied anode potential. With other metallic electrodes this dependence cannot be observed, as their potential rises rapidly from the low value at which the anode is dissolved, to higher values because the metal of the anode is gradually rendered passive; therefore, the potential at such anode cannot be regulated and maintained within the required limits. Another analogy connected with the reduction process can be found in the fact that oxidation yields are proportionally higher with an increased oxygen overvoltage of the applied anode; generally, the most efficient oxydation will be therefore found with platinum and lead (or rather PbO_2), while nickel electrodes will show a comparatively low oxidation efficiency. This analogy, however, is not generally valid because contrary to all expectations processes are known, which proceed most effectively with metals having low oxygen overvoltage. Higher concentration of depolarizer supports the yields, in the same way as sometimes even increased temperature. Electrolytic oxidation is further facilitated by the presence of catalysts in the solution which can exist in two valency states. These are salts of cerium, titanium, vanadium as well as ferricyanides and chromates; the most efficient are cerium salts. The action of these substances is most probably the same as cathodic catalysts. A small admixture of fluorides too will sometimes

favourably influence the increased yields, especially in the case of oxidation of sulphates to persulphates, and of iodates to periodates. The part played by fluoride is not definitely known; it would appear that this substance increases the anode potential which in turn increases the yields of the reactions in question.

The polymerization of anions is a special type of irreversible anodic processes. Of these the oxidation of sulphate to persulphate ions has been studied in the deepest detail. In the production of persulphuric acid the yield is increased to a certain limit by a higher concentration of the initial sulphuric acid and an increased current density at the anode of smooth platinum. In too concentrated sulphuric acid the persulphuric acid is already hydrolysed to a considerable extent to monopersulphuric acid (Caro's acid), which then acts as a depolarizer and lowers the required high potential at the anode. Electrolysis of sulphate solutions also gives persulphates and in this reaction the current efficiency will depend on the nature of the cation; the efficiency increasing in the order of Na^+, K^+ and NH_4^+.

Formerly the formation of persulphate was attributed to the polymerization of HSO_4 radicals, formed by the discharge of bisulphate ions:

$$HSO_4^- \rightarrow HSO_4 + e$$
$$2HSO_4 \rightarrow H_2S_2O_8.$$

This theory accounts for the dependence between the current efficiency and the concentration of HSO_4^- ions present in the solution. It cannot explain, however, why the yields at the electrolysis of solutions of sulphates, in which the concentration of HSO_4^- ions is very low, are even greater than when electrolysing solutions of sulphuric acid alone or its mixture with a sulphate. This deficiency is not found in the recent explanation of the reaction mechanism, according to which the sulphate ions SO_4^{--} are primarily oxidized by hydrogen peroxide or by hydroxyl radicals formed, according to equations:

$$H_2O = OH + H^+ + e$$
$$2\,OH = H_2O_2$$
$$2\,SO_4^{--} + H_2O_2 = S_2O_8^{--} + 2\,OH^-$$

or

$$SO_4^{--} + OH = SO_4^- + OH^-$$
$$2\,SO_4^- = S_2O_8^{--}.$$

Reactions of the same type are the anodic oxidation of thiosulphate, sulphite, carbonate and phosphate ions, proceeding according to overall equations:

$$2\,S_2O_3^{--} \rightarrow S_4O_6^{--} + 2\,e$$
$$2\,SO_3^{--} \rightarrow S_2O_6^{--} + 2\,e$$
$$2\,CO_3^{--} \rightarrow C_2O_6^{--} + 2\,e$$
$$2\,PO_4^{---} \rightarrow P_2O_8^{--} + 2\,e$$

With these processes a similar reaction mechanism as with sulphate oxidation is assumed. This opinion is verified also by the observation that the presence of substances catalysing the hydrogen peroxide decomposition (iron, copper and manganese salts and finely dispersed platinum) inhibit almost entirely the proceeding of the oxidation in the required direction.

The oxidation of salts of trivalent chromium into chromates and of iodate into periodate proceeds in a different manner; in these processes the lowest yields are obtained at smooth platinum, better ones at platinum coated with platinum black, and the highest ones at lead covered with lead dioxide. Yields are also increased by higher temperature and alkalinity of the electrolyte, i. e. by factors which suppress the polymerization of the mentioned anions. It has been proved by experiment that the actual oxidizing substance in this instance is not the hydrogen peroxide or hydroxyl radical but an oxide of the metal applied as the anode. Since chromates and iodates are reduced by hydrogen peroxide it can be expected that the conditions under which peroxide is decomposed or which facilitate the formation of molecular oxygen from the hydroxyl radical, will lead to increased yields of the required products. In agreement with this assumption the yields increase with a higher temperature, alkalinity of the solution and by the application of an electrode coated by finely dispersed platinum or lead dioxide which catalyse perfectly the hydrogen peroxide decomposition.

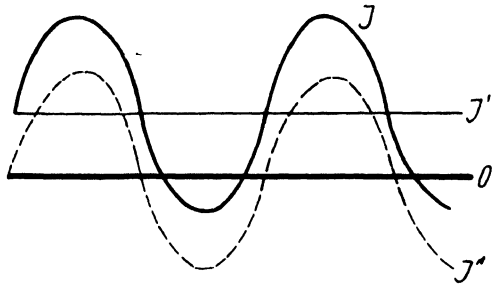


Fig. 34. Superposition of alternating current on direct current.

A very interesting example of an anodic process is the manufacture of insoluble compounds, produced by metallic ions, formed during the dissolution of the electrode which after entering the solution react with such anions with which they precipitate in the form of poorly soluble salt. The formed precipitate is very often deposited on the anode and being a poor electric conductor it prevents the flow of current.

To remedy this hindrance two methods can be used. When alternating current I'' with a higher peak intensity is superimposed on the electrolysing direct current I', alternating current I will result, which is displaced in respect of the zero line so that in one half of the period (the positive one) more current will pass than in the second, negative half (see Fig. 34).

During the positive half of the period cations will enter the solution which after reacting with the anions will be deposited as insoluble precipitate at the electrode; a small quantity of hydrogen will be evolved under the precipitate layer during the passage of the negative wave and will throw it off.

The same result will be obtained if the precipitating anions are allowed to react with the cations in the bulk of the solution only, and care is taken to prevent them doing so closely round the electrode.

For this reason the concentration of the anions has to be kept at a low value by the gradual addition of the respective salt to the solution, i. e. at a rate corresponding to its consumption for the precipitation of the insoluble salt. In addition, another anion is added to the electrolyte in a higher concentration which forms with the metallic cation a soluble compound the function of which is the conduction of current. The precipitating anions in the course of electrolysis are quickly consumed at the anode so that the actual conducting of current to the electrode is then carried out almost exclusively by the other anions. The cations not precipitated by the latter anions can then migrate into the bulk of the solution, where they meet the precipitating anions and form insoluble compounds.

Electrolytic production of white lead is based on this principle; during this process the lead anode is immersed in a solution of alkali chlorate or acetate with a small quantity of alkali carbonate. In the course of electrolysis the lead is dissolved and forms at first a soluble chlorate or acetate: the ions Pb^{++} diffuse and migrate into the bulk of the solution where the necessary amount of OH^- and CO_3^{--} ions is found with which they react and precipitate as insoluble, basic lead carbonate. The solution is thus deprived of the carbonate ions which are then supplemented by a continuous absorption of carbon dioxide in the electrolyte. By using chromate, instead of carbonate chromium yellow is formed. Analogously also zinc white could be produced.

For anodic processes the choice of materials for the electrode is much more limited than for cathodic ones, as the anode could be easily attacked by the products of the electrolysis (chlorine, oxygen etc.), or electrochemically dissolved. In alkaline solutions the selection will be restricted to the application of platinum (or alloys of platinum with irridium or rhodium), palladium, carbon (or rather graphite) iron and nickel, while for acid solutions only metals of the platinum group and graphite will be suitable; in a special case of the electrolysis in sulphuric acid solutions lead has found wide use, it getting coated with a conductive film of lead dioxide.

In anodic oxidations is is often necessary to take precautions to prevent or at least check the reduction of the oxidation product at the cathode. To this end diaphragms or high cathodic current density are applied respectively. Cathodes made of metals with low hydrogen overvoltage may also restrict the undersirable reduction. A special type of diaphragm is produced by adding to the electrolyte a small amount of alkali chromate when working with a neutral or weak acid solution. The chromate will be reduced at the cathode giving an insoluble chromic salt which envelops the electrode in the form of a thin film which acts as a diaphragm.

Compared with reduction processes the importance of electrochemical reactions carried out at the anode in inorganic chemistry is incomparably higher.

By this method many economically very important products and basic raw materials, indispensable for the modern advanced standard of industry are produced on a commercial scale (chlorine, fluorine, hydrogen peroxide, chlorates, potassium permanganate etc.).

VIII. CONSTRUCTION OF ELECTROLYTIC CELLS FROM THE GENERAL POINT OF VIEW

Although every electrochemical process requires special equipment which permits the most economical manufacture and use of raw materials and energy, there are many similar constructional elements which will be of advantage to discuss before passing on to individual processes.

A. ELECTRODES

The direct current is conducted to and from the electrolyzed solution by means of electrodes. Chemical reactions proceed at the electrodes and electric energy is consumed. The electrode connected to the negative pole of the current source is called the cathode; it is the electrode through which the electrons enter the electrolyte or through which the "positive" electricity leaves the solution. The electrode connected to the positive pole of the current source is called the anode; it is the electrode through which the electrons leave the solution to return to the source of current or through which the "positive" electricity enters the solution.

1. Connection of the electrodes

As a rule an electrolytic cell (electrolyzer) contains several electrodes. Depending on the kind in which the electrodes are connected to the source of the current we speak of either monopolar or bipolar electrodes.

In the case of a monopolar connection each electrode has only one polarity, i. e. it functions as either anode or cathode. All electrodes of the same polarity (in one electrolytic cell) are connected in parallel. The resultant voltage E across the whole electrolytic cell equals the potential difference between any anode and any cathode (see Fig. 35). The current passing through the electrolyzer is regulated according to the sum total of the surface area of all electrodes of one polarity. Thus a characteristic feature of electrolyzers with monopolar electrodes is the strength of the current many times greater than the voltage. It is a matter of technical practice to connect a number (n) of such electrolytic cells in a series connected to a source of direct current which has a voltage $E_c = nE$.

A bipolar electrode (plate-shaped in most cases) is characterized by the fact

that one side of it functions as an anode and the other as a cathode (see Fig. 36). In the case of a bipolar arrangement of an electrolyzer containing m electrodes only the terminal electrodes are connected to the source of the current. The electrons enter the solution through one terminal electrode (the cathode) and are transferred in the form of ions to the next electrode not connected to the

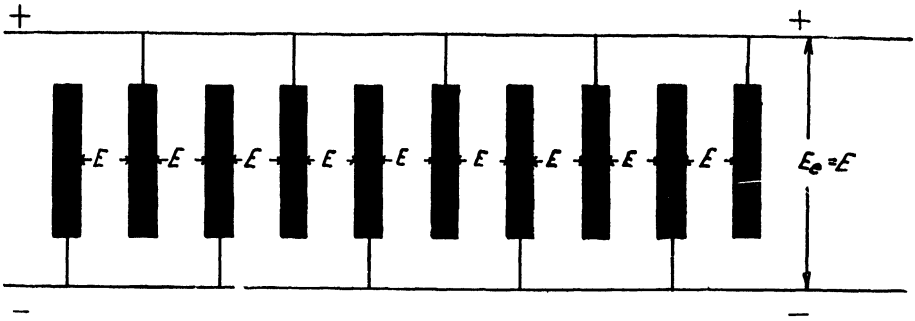


Fig. 35. Diagram of a monopolar connection

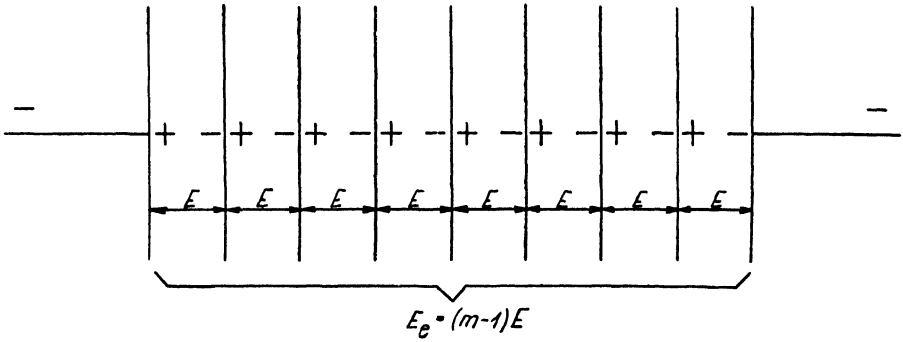


Fig. 36. Diagram of a bipolar connection.

current source. There they leave the electrolyte being transferred onto the electrode, thus giving this side of the electrode the character of an anode. Any further passage of the electrons is only possible through the electrode from which they enter again the solution in the form of ions. This side of the electrode consequently acts as a cathode. In this way the electrons pass through all electrodes and finally they leave the cell through the last electrode which is connected to the source of the current. This terminal electrode acts then as a monopolar anode.

Should the operating voltage between two neighbouring electrodes equal E

then the voltage across the whole electrolytic cell is expressed by the product $E_e = (m-1)\,E$, m being the number of electrodes connected in series. The electrolytic cell usually consists of such a number of electrodes that its resultant voltage equals the normal voltage of the external source of the current. It is of course also possible to connect n electrolytic cells with bipolar electrodes in series so that the total voltage of such a system equals $E_e = n\,(m-1)\,E$. The current passing through a bipolar electrolytic cell is regulated according to the surface area of one electrode. In comparison with monopolar electrolytic cells the current is here generally weaker while the total voltage across the bipolar electrolytic cell is much higher.

In many electrometallurgical refining processes impure metal is dissolved electrochemically at the anode and deposited at the cathode in its pure form. Thus, in the case of a monopolar connection the weight of the anode decreases while the weight of the cathode increases. On the other hand the weight of bipolar electrodes remains practically constant apart from a slight loss due to the separation of impurities which constitute the anode slime. The composition of a bipolar electrode, however, does change in the course of electrolysis because on the anode side the impure material enters the solution to be deposited in its pure form on the cathode side. The electrode consists at the beginning of the refining process solely of crude metal; the thickness of the impure metallic layer decreases during electrolysis and the layer of pure metal on the other side of the electrode increases. Electrolysis is terminated when the crude metal on the anode side is practically dissolved; the remnants are then stripped from the plates of the refined metal.

2. Arrangement of electrodes in the electrolytic cell

With few exceptions the electrodes in electrolytic cells are arranged either vertically of horizontally. There is no exact rule as to which particular arrangement should be used as the position of the electrodes depends on the specific nature of the electrolytic process involved. Nevertheless, certain general rules may be laid down.

When in the electrorafination of metals (e. g. copper) the impurities accumulate in the anode slime at the bottom of the tank, a vertical arrangement of electrodes is more suitable than a horizontal one, particularly when the process is not accompanied by an appreciable evolution of gases.

The same arrangement is applied for electrometallurgical processes where insoluble anodes are used and the liberated gas is allowed to escape freely into the atmosphere.

Sometimes the refined metal is not deposited in a compact form but as loose crystals (e. g. silver). In this case both vertical and horizontal electrodes can be used with equal success.

Both types of electrodes are successfully used in the large-scale manufacture of inorganic compounds. The choice of arrangement also depends on various

other circumstances, i. e. whether a diaphragm is used for the process or not, whether gases are liberated and collected, whether the products of electrolysis are allowed to accumulate in the solution, whether the electrolyte circulates, whether the solution is resaturated in the electrolytic cell itself or externally, whether mercury is used as a cathode etc. In general, vertical electrodes are preferred whereever possible as they are more easily connected to the conductors and the cell requires much less floor space.

3. The shape of electrodes

Plates, sheets, rods, tubes, wires and gauzes may be used for electrodes. Plates are the most widely used. Metal cathodes and insoluble metal anodes are generally made of rather thin sheets; thicker plates are only used for making soluble metal anodes and electrodes of nonmetallic material. Rod-shaped electrodes are hardly ever used. They are only used in cases where plates would

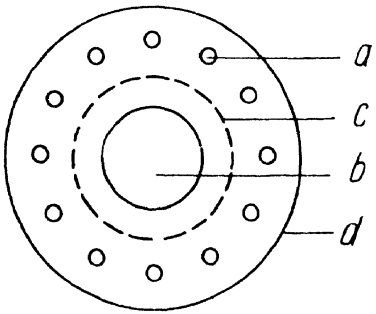


Fig. 37. Schematic arrangement of rod-shaped electrodes in a cylindrical electrolytic cell:
a — rod-shaped electrodes, *b* — central electrode, *c* — diaphragm, *d* — jacket of the electrolytic cell.

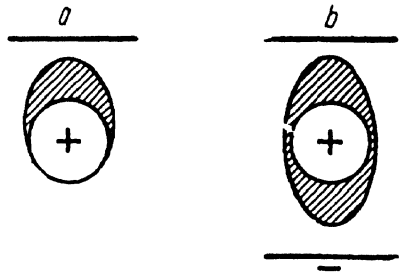


Fig. 38. Schematic diagram of distribution of current density at a rod-shaped electrode.
a — with one oppositely charged electrode, *b* — with two oppositely charged electrodes.

be technically difficult to make (magnetite electrodes). Occasionally, rod-shaped electrodes are preferred especially when an electrolytic cell has to be cylindrical (see Fig. 37).

Often graphite plates are used as anodes (e. g. production of hydroxides) with short graphite stems screwed into then. These short stems merely serve as conductors.

Rod-shaped electrodes — if used in a great number and connected to a common source of the current — have a drawback because great care must be taken to ensure good contact at each single electrode; otherwise some would have an insufficient current load and some would be overloaded. Also the current density is not uniformly distributed around them. Surface areas of the

rod-shaped electrodes, which are nearer to the neighbouring oppositely charged electrode, show a greater current density than the rest of the electrode surface (see Fig. 38).

Tube-shaped electrodes are usually not used in the electrolytic cells. Lead dioxide electrodes serve as a rare example; these may be produced by an electrochemical deposition of lead dioxide on a graphite rod. When electrolysis is terminated the graphite core is removed by drilling so that the remaining tube consists only of lead dioxide. Sometimes, however, cylindrical electrodes are used which are made of a thin metal sheet rolled into a wide cylinder. In certain rare cases the inner surface of a cylindrical electrolytic vessel can also function as an electrode.

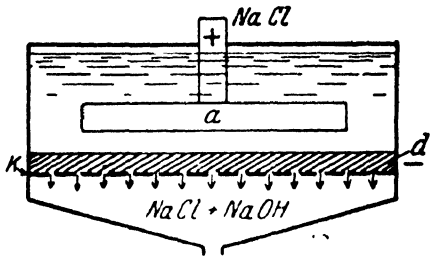


Fig. 39. Electrolyzer with horizontal diaphragm supported by a wire-gauze electrode (cathode).
a — Anode, *d* — Diaphragm, *k* — Cathode

In other cases electrodes are made of wire-gauze. Where the cost of material is not essential the wire-gauze is made of thick wire. Such wire-gauze electrodes are used, e. g. in the production of caustic by the diaphragm method. In this process they make possible the easy removal of the produced caustic solution from the cathode space (See Fig. 39.).

In the case of expensive materials (platinum, platin-irridium), however, the wire-gauze is made of thin wires (e. g. the production of bleaching liquors by the Kellner process). For laboratory purposes the thin platinum wires are sealed into a glass tube. The platinum is connected to the copper lead-in wire by a weld or by mercury. For large — scale production foils are preferred as they are more economical because they give a maximum effective electrode surface area at a minimum weight. The foils are fastened by platinum wires to a supporting bar made of copper or aluminium which has a coating of natural or synthetic rubber to avoid corrosion by the electrolyte; the supporting bar also serves as a lead-in conductor (see electrodes for preparation of persulphates).

4. Materials for electrodes

As far as their function is concerned, electrodes may be divided into two groups:

a) Anodes of crude metal which is to be electrolytically refined and cathodes of the same refined metal. Electrometallurgical refining processes in aqueous solutions belong to this group (refining of Cu, Ag, Pb, Ni, Fe etc.).

b) No electrode changes electrochemically during the electrolysis — or at least one remains unchanged. An example of an unchanging anode (indifferent anode) can be found in the electrolysis of zinc sulphate with an aluminium

cathode and insoluble lead anode. On the other hand, in the electrochemical preparation of white lead the cathode remains unchanged while the anode dissolves.

The second group of electrodes is employed mainly in processes used in inorganic chemical industry. The choice of electrically conductive materials that resist attack by electrolyzed solution is very limited. From materials which are liquid at a normal temperature only mercury can be used as an electrode (production of hydroxides). Solid metals which can be used as electrodes are: iron, nickel, aluminium, copper, lead, platinum (or its alloys with irridium) and tantalum. Iron is suitable for electrodes in alkaline solution (see electrolysis of water). Nickel is even more resistant than iron to corrosion by alkaline electrolytes. Aluminium is used but rarely (for example as cathode starting sheets for the electrochemical deposition of zinc). Copper cathodes were only used in some of the first electrolytic cells for the preparation of hydroxides by the diaphragm method. Lead has found wide use as an insoluble material, mainly for anodes in solutions of sulphuric acid, sulphates and chromates. In such electrolytes the sheet of lead applied as anode receives a coat of thin conductive film of lead dioxide formed during the electrolysis. The use of platinum is limited nowadays, due to the prohibitive price, to such processes where its oxygen overvoltage, highest among all other metals, is decisive (the preparation of perchlorates and persalts). Tantalum receives a thin nonconductive oxide coating if used as anode; it is sometimes used as a reinforcement for platinum foils.

From among metallic oxides lead dioxide, ferrous-ferric oxide (magnetite and manganese dioxide are used for manufacture of electrodes. The difficulties encountered in preparation of compact electrodes of lead dioxide prevented the practical application of this material. The same holds good for manganese dioxide which would be otherwise, being an anodically insoluble substance, an excellent electrode material for some processes. A comparatively larger use is made of magnetite which has proven its value in some plants as anode material in the manufacture of chlorates. Magnetite electrodes are produced by melting magnetite under addition of a suitable flux or by partial reduction and fusion of ferric oxide in an electric furnace or finally by burning iron in oxygen. Such electrodes are available in shapes of rods, tubes, flats tiles or strips. The material is very brittle and also current connections are difficult to make.

Among the nonmetallic materials suitable for the manufacture of electrodes let us mention carbon and graphite. It is only graphite, however, which has found a practical application because its mechanical and chemical resistance when used as anode exceeds by far that of the amorphous carbon. Another great advantage of graphite is its easy machinability and the possibility of arranging a reliable connection to the source of current. Though graphite used as anode manifests a very good resistance, it has a limited service life. Its deterioration is due to the pores which constitute 19 to 26 per cent of its total volume. Inside the pores filled with the electrolyte there proceeds the electro-

lysis with a considerable evolution of oxygen; as a result, graphite is oxidized to carbon dioxide. To prevent the disintegration of graphite it has been proposed to clog the pores by a filler (such as paraffin, tar, naphtaline, chlorinated naphtaline, mineral waxes, silicon dioxide, etc.). Actually, this method gave no satisfactory results. If nowadays tar is used as filler sometimes, it is only to prevent thus the electrolyte from creeping along the graphite surface up to the copper sleeve, by which the electrode is connected to the source of current; otherwise, after some time, this connection would be destroyed by corrosion.

5. Connection of electrodes to the source of current

The current is carried to the electrolyzer by copper or alluminium busbars from which it is distributed by cables or by a system of elastic copper lamellae to the terminals of the electrodes. The current passes through many points of contact which determine the magnitude of so called contact resistance. The more imperfect are the contacts at these points the greater the losses in electrical

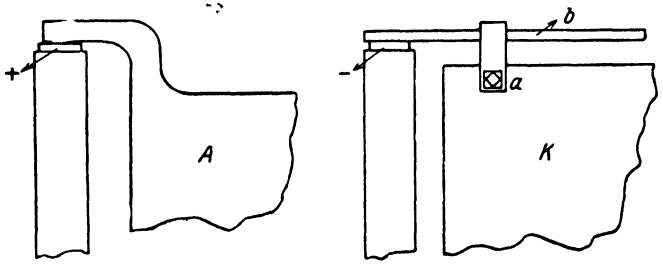


Fig. 40. Schematic representation of the contact obtained by the weight of the electrode.
a — Anode, *d* — Diaphragm, *k* — Cathode.
Anode lug *A* and carrier bar of cathode *B* rest upon a copper strip conductor.

energy that is converted into Joule's heat. Losses due to imperfect connections may amount to 10 to 20 per cent of the total energy required for the electrochemical process. It is therefore necessary to give proper care to both design and maintenance of contacts.

The design of connection of the electrodes to the current conductors depends on the nature of the process. There is a considerable difference between the connections used in electrolyzers where periodical removal of electrodes from the bath is required and the connections used in electrolyzers where the electrodes are not removed and form a fixed part of the equipment. The first case is encountered mainly in electrometallurgical refining processes where anode scraps and cathodes with the deposited metal are removed. In such cases

contacts are provided by the mere pressure of the weight of the electrode upon the connecting busbar. Such a design used in refining of copper is illustrated in Fig. 40; the anode has a lug pressed by its weight against a copper strip conductor; analogously the contact of the cathode plate is obtained by means of the yoke *a* and carrier bar *b*.

The way of connecting the current conductors to electrodes which remain permanently dipped into the solution of electrolytes depends on the material of the electrode (whether nonmetallic, such as graphite, or metallic.) One possible method of connecting a graphite rod to the current conductor is schematically represented in Fig. 41.; the upper end of the electrode has a small recess; it is encompassed by a two-piece copper terminal which is connected to the current conductor. A terminal for connection of a plate shaped electrode to the current conductor is illustrated in Fig. 42. At first the upper edge of plate *A* is fitted

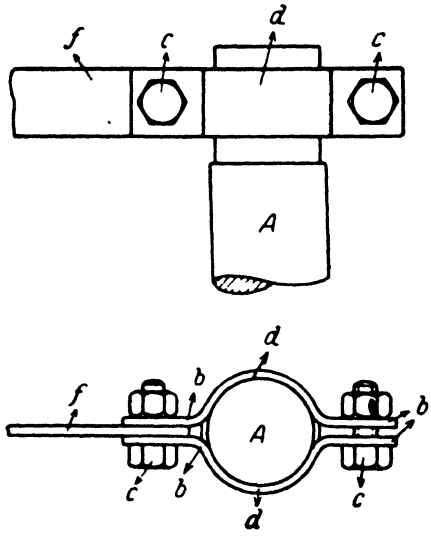


Fig. 41. Connection of a graphite rod electrode to the current conductor:
A — graphite electrode, *b*, *d* — two-piece copper terminal, *c* — clamping bolts, *f* — current conductor.

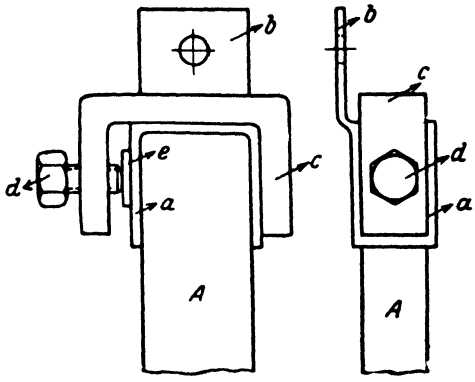


Fig. 42. Connection of a graphite plate electrode to the current conductor:
A — electrode, *a* — stirrup, *b* — stirrup extension and lead-in conductor, *c* — second stirrup, *d* — clamping bolts, *e* — contact plate.

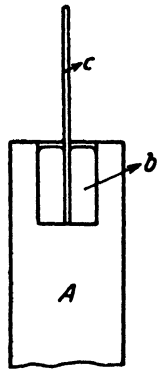


Fig. 43. Connection of a graphite electrode to the current conductor:
A — electrode, *b* — filling metal *c* — current conductor.

with the stirrup *a* the extension of which *b* serves for leading-in the current. The second stirrup *c* carries the bolt *d* which presses the contact plate *e* against the first stirrup. Sometimes the current conductor is connected to graphite using molten metal (see Fig. 43). A hole is drilled into the graphite *A*, then the metal conductor *c* is inserted into this hole and the remaining space is filled up by molten metal (such as copper, bronze, solder or easily fusible alloy consisting of 8 parts of bismuth, 3 parts of tin and 5 parts of lead).

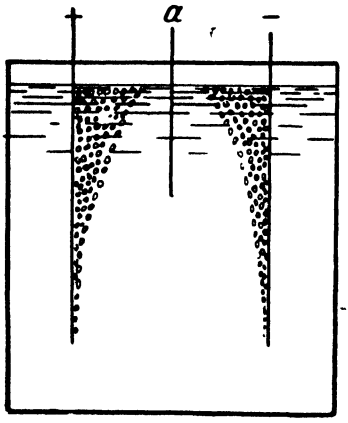


Fig. 44. Electrolyzer with a partition to prevent the mixing of gaseous products of electrolysis.

The connection of metal electrodes to the source of current can be made in a much simpler way using bolts, revets, welding, brazing, soldering etc. In case of wire gauze electrodes usually spot contacts are not satisfactory but the wire-gauze should be welded to a metal frame all around; the current is then led into this frame.

B. DIAPHRAGMS

The anode and cathode compartments in an electrolyzer are sometimes separated by a partition called diaphragm. The electrolyte around the anode is called the anolyte, and the one around the cathode a catholyte. The purpose of the diaphragm in the best sense of the term is to separate individual gaseous or solid products of electrolysis. When water is electrochemically decomposed vertical electrodes are exclusively used and an asbestos partition or an iron or nickel gauze is suspended to a certain height in the electrolytic vessel to prevent mechanical mixing of hydrogen and oxygen (see Fig. 44).

When this kind of diaphragm is used the composition of both anolyte and catholyte is the same. Similar conditions hold good for the electrolytical refining of certain metals when the slime formed on the anode which contains precious metals is caught in a cloth bag covering the anode (e. g. when refining silver).

By diaphragms in a narrow sense we also understand a kind of partition which prevents as much as possible the diffusion of dissolved products of the electrolysis from one electrode to the other but must not hinder the passage of ions migrating under the influence of the electrical field; in other words this partition should possess a high diffusion resistance but a low electrical resistance. Unless mutual diffusion and the mechanical mixing of anolyte and catholyte are prevented, i. e. on electrolyzing a solution of common salt, a mutual reaction occurs between the products of electrolysis, namely chlorine and hydroxide in which case hypochlorite ions are formed. They can then be converted, either electrochemically or chemically to chlorate ions. On separating both electrodes

by a porous diaphragm any mutual reaction of the products of electrolysis is rendered impossible; therefore at the anode chlorine is liberated and in the catholyte hydroxide can accumulate up to a certain concentration. The electrochemical oxidation of chromic salts to chromates is another example; the diaphragm prevent the diffusion of chromate ions to the cathode where they would be reduced.

A diaphragm having a low electrical resistance and at the same time a high diffusion resistance is difficult to make, as a diaphragm with wide and short pores has both electrical and diffusion resistance lower than a diaphragm with long and narrow pores.

Needless to say the diaphragm must be resistant to the corrosive action of both electrolyte and electrolytic products. This requirement is also difficult to comply with when the diaphragm is in contact with an acid anolyte and an alkaline catholyte.

Diaphragms which resist hydroxides are made of asbestos, mixture of asbestos and kaolin, soapstone, cement etc. Fused alumina (corundum), quartz, glass, highly burnt fire clay, strong acid clays and such like substances are used for acid resisting diaphragms. The required degree of porosity is attained either by casting without binder and subsequent burning or by adding certain substances to the diaphragm mass which are removed by burning. Salt is added to the cement diaphragm in the course of production which is then leached out. Fine sawdust can also be added to the mass and burnt out subsequently.

Diaphragms are made in the form of plates or prisms with bottoms; tubes and cylinders can also be used. If a diaphragm larger than commercially available is required small plates are used and cemented together in a key-joint.

A special type is the filtering diaphragm; it must be permeable both for migrating ions and for the electrolyte. Such a diaphragm is used in the Siemens and Billiter electrolyzer for production of hydroxides; a paste made of asbestos fibres and baryte powder is spread over a horizontal iron gauze that serves as a cathode. The electrolyte percolates, with a certain velocity, through this filtering diaphragm and comes in contact with the cathode where an alkali hydroxides solution is formed. This caustic solution drops through holes in the electrode to the bottom of the electrolyzer from where it is taken off.

C. ELECTROLYTIC VESSELS

1. Shape of vessels

Electrolytic vessels for unipolar electrodes have usually rectangular or square cross sections. These electrolyzers can be either closed or open. This depends on whether gaseous products are to be collected or not.

Cylindrical electrolyzers are used only exceptionally because of floor-space economy. Their application is justified only in cases where diaphragms of the required quality are available only in cylindrical form, or in cases where dif-

ferent current densities at both electrodes and uniform distribution of current are to be maintained.

Bipolar electrodes are suspended or inserted into an oblong vessel of rectangular cross section or arranged to form the so called filter press cell. The first method is used mainly for the electrolytical refining of metals where the crude metal dissolves at the anode and is deposited at the cathode in pure form; the potentials on both sides of the bipolar electrode are equal but of opposite sign, and so they cancel each other. The current flowing through such an electrode has only to overcome the insignificant ohmic resistance of the electrode. Compared with this the resistance of the electrolyte is much greater and so in this case the electrodes can be arranged at a certain distance from the walls of the vessel without causing any appreciable loss of current, which may by-pass the electrodes.

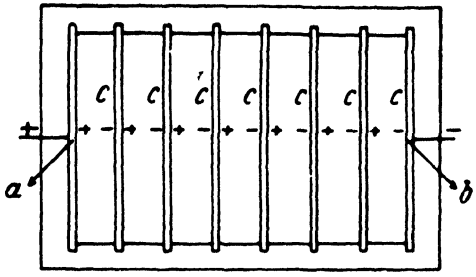


Fig. 45. Schematic diagram of an open type electrolyzer with bipolar electrodes inserted into grooves in nonconductive walls of the vessel.

a, *b* — metal (monopolar) terminal electrodes, *c* — bipolar electrodes

The possibility of the free suspension of the electrodes in a vessel is of great help in metallurgical refining processes where both anodes and cathodes have to be periodically removed from the electrolytic bath and replaced.

A different arrangement is to be used for electrolysis in which the anodic and the cathodic processes are of a different character (e. g. decomposition of water) so that the unequal potentials at both sides of the bipolar electrode do

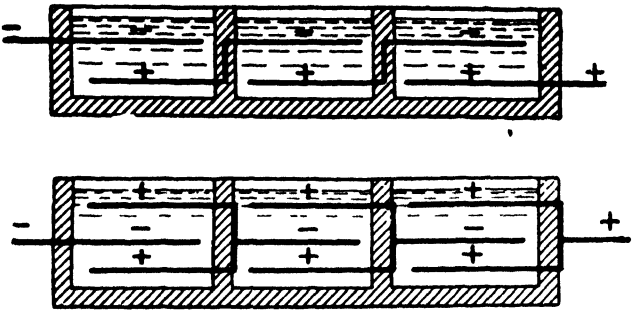


Fig. 46. Schematic diagram of an electrolyzer with partitions and horizontal bipolar electrodes.

not cancel each other but result in a definite final polarization voltage acting against the electrolyzing voltage. In this case the resistance offered by the electrolyte is less than the resistance which the current has to overcome on passing through the electrode; it is evident, that the electrodes must be close

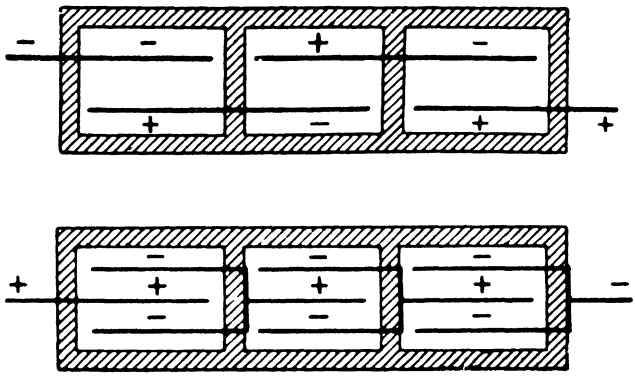


Fig. 47. Schematic diagram of an electrolyzer with partitions and vertical bipolar electrodes.

to the walls of the vessel. This is generally done by inserting the electrodes into grooves in the walls of the vessel and sealing them by a suitable cement; the walls of the vessel must be nonconductive, to prevent a short-circuit between the electrodes (Fig. 45). The same effect can be attained if the vessel is divided by a suitable number of nonconductive partitions through which the bipolar electrodes pass, as shown in Figs. 46 and 47.

Filter-press electrolyzers, which are similar to a plate and frame filter press, are sucessfully used when gases are evolved in course of the electrolysis. Some designs of these types of electrolyzers will be described in detail in the chapter dealing with the electrolysis of water. The electrolyzer consists of number of frames with bipolar plate electrodes *c* which are separated by diaphragms *d*. Frames and diaphragms are tightened by bolts between the front plates *a*

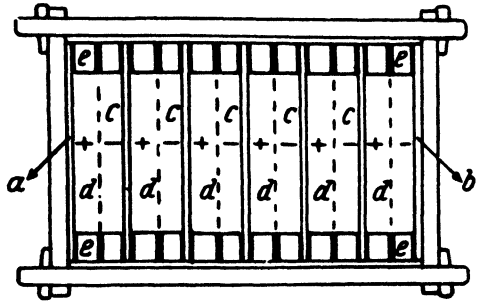


Fig. 48. Schematic diagram of a filter-press electrolyzer.
a, b — Monopolar terminal electrodes, *c* — Bipolar electrodes, *d* — Diaphragms, *e* — Filter-press frames.

and *b* which are connected to the source of current (see Fig. 48); in this way a series of chambers is formed and each of them functions as an independent electrolyzer. Each frame has holes through which make-up electrolyte is led in and through which the evolved gases are drawn off together with the residual electrolyte. The holes are arranged in such a way that the electrolyte flows through the cell diagonally.

2. Materials used for the construction of electrolytic vessels

The selection of material must be made with due regard to the composition and temperature of the electrolyte. Suitable materials are metals, stoneware, porcelain or glass, concrete, wood and different rocks such as granite, sandstone or syenite. Iron is most often used, namely if the electrolyte has an alkaline reaction or a passivating effect upon iron (for example in chromium plating bath). Stoneware or sometimes porcelain are suitable materials for electrolytic cells to be filled with acid solutions. The dimensions of vessels made from these materials are limited because large vessels are difficult to produce and the volume of the bath rarely exceeds 1 cu. m. The stones mentioned are suitable for acid electrolytes at higher temperatures but they imply a disadvantage as such an electrolytic cell cannot be made of one piece but has to be assembled of individual plates. The seams are sealed by a suitable cement, the whole being secured by an outer iron jacket. Wood (pine or larch) can only be used for weak acid solutions. This is used for manufacture of large vessels which cannot be made of stoneware. Wooden electrolytic vessels and concrete vessels have usually a mild-steel reinforcement.

Sometimes the vessels are lined with a corrosion resisting material (lead, tiles, cement, tar, asphalt, rubber or synthetic resins). Lead is used to line both wooden and steel vessels; enameled steel vessels are sometimes used in small plants if electrolysis is to proceed at a higher temperature. Acid proof tiles used for the lining of steel vessels are mounted on a cement basis. A coating of tar or asphalt can sometimes be used to line a wooden container instead of the more expensive lead. Steel electrolyzers are frequently used with a natural or synthetic rubber lining.

3. Covers of electrolyzers

When it is necessary to collect the gases liberated during the electrochemical process because they are either the product required or a troublesome byproduct, the vessel is closed by a suitable cover which usually is used to support the electrodes. In the case of the filter-press electrolyzers with bipolar electrodes the top of the frames usually serves as a cover. Electrolyzers with monopolar electrodes are closed by covers made of steel, concrete, cement, stoneware, etc. Seals between covers and vessels or electrodes are made of asbestos cord, bitumen, asphalt, mixture of kaolin and tar, cement, synthetic resins, etc.

D. MOTION OF ELECTROLYTE

In most electrolytical processes there must be a uniform motion of the electrolyte in order to prevent concentration polarization and non-uniform distribution of current density at the electrodes which can be caused by different concentrations in the various layers of the electrolyte.

In electrolyzers where during the operation no replacement of the electrolyte is required (e. g. electrometallurgical refining processes) mixing can be carried out by a suitably designed stirrer or by gas (air) which is led in through a perforated pipe which reaches to the bottom of the vessel. The problem of mixing is less difficult in processes when gases are liberated at the electrodes. If the ascending bubbles of liberated gases do not secure a sufficient circulation an arrangement is applied as shown in Fig. 49. Vessel *a* is divided by two longitudinal nonconducting partitions *b* into the electrolytical section proper and two side sections. Bipolar electrodes *c* are inserted into the grooves of the partition walls. Hydrogen liberated in the individual compartments rises and carries with it the electrolyte which then flows over the upper edge of the electrodes; in the side sections the liquid is separated

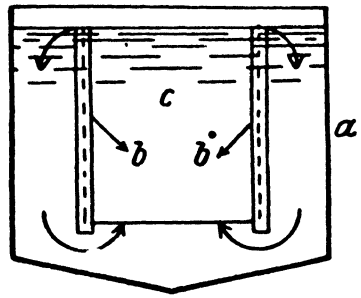


Fig. 49. Device for intensive mixing of electrolyte by means of gas bubbles evolved in the course of electrolysis:
a — Electrolytic vessel, *b* — Longitudinal nonconducting walls with grooves for electrodes, *c* — Bipolar electrodes.

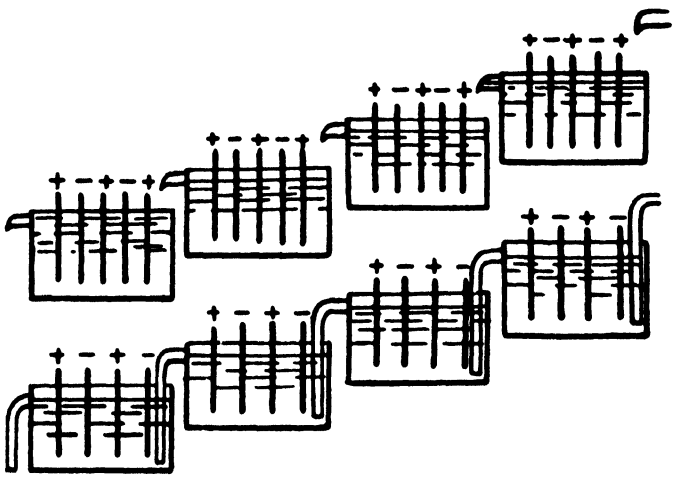


Fig. 50. Schematic diagram of a series of cells arranged in cascades.

from the gas and owing to its slightly higher specific gravity sinks to the bottom of vessel *a*, enters the central section again, and the cycle is repeated.

If for any reason electrolyte has to be continually removed and replaced, another system of agitation is used. By one method electrolytic cells are connected in cascades, so that the electrolyte flows by gravity from one cell to another either to the level or to the bottom of the next cell below (Fig. 50).

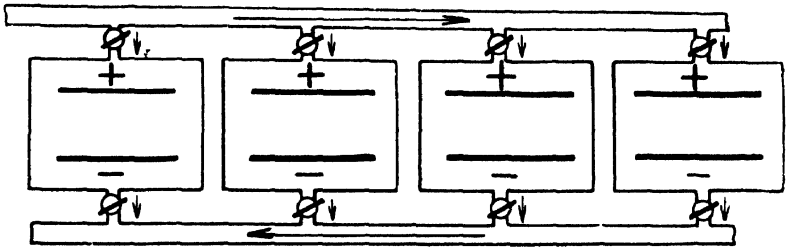


Fig. 51. Schematic diagram of a parallel hydraulic connection.

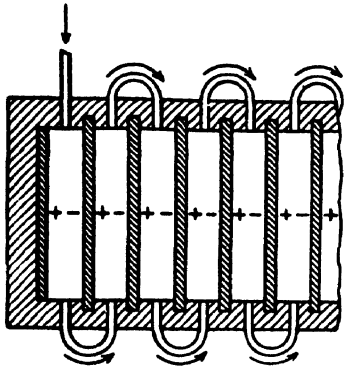


Fig. 52. Hydraulic connection in series of cells with bipolar electrodes.

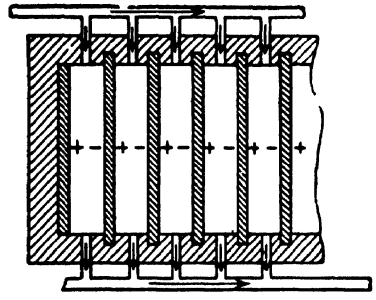


Fig. 53. Hydraulic connection in parallel of cells with bipolar electrodes.

A parallel connection of cells can be achieved by the application of a manifold and collecting tube for the feeding and draw-off of the electrolyte, respectively, as shown in Fig. 51.

In the case of bipolar electrodes the individual cells can also be connected in series (Fig. 52) or in parallel (Fig. 53).

The same is valid for individual cells of the press-filter type electrolyzer; they can also be hydraulically connected in series or in parallel. In the case of a connection in series the inlet and outlet openings are alternately connected in pairs; in the case of a connection in parallel all openings on one side of the frame are connected so that they form a channel.

E. REMOVAL OF GASES EVOLVED ON ELECTROLYSIS

If useless but harmful gases escape on electrolysis various types of equipment may be used to remove them; one device of this kind is illustrated in Fig. 54.

Pipe *a* is arranged along the longitudinal wall of the vessel and is connected to a vacuum pump. The exhausted gases are led through pipe *b* to special separating vessels to remove the droplets of electrolyte entrained. Sometimes the baths are covered by hoods made of glass, sheet metal or plastics and the gas is exhausted from the hoods.

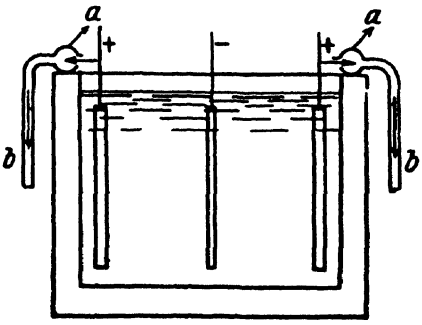


Fig. 54. Schematic diagram of a device for sucking off gaseous products of electrolysis. *a* — Suction tube, *b* — Gas outlet pipe.

F. ELECTROLYTE WARMING AND COOLING EQUIPMENT

If electrolysis is to proceed at a higher temperature Joule's heat evolved during the flow of the current through the electrolytic cell is utilized for warming up the electrolyte to the temperature required. Should this prove insufficient, or in cases where Joule's heat cannot be used for some reasons, special heating devices must be employed. Heating devices installed outside the electrolyzer are suitable for open containers and not too high temperatures. Such heaters are installed before the first cell in an arrangement of cascades with a circulation of the electrolyte. The electrolytic cell can also be provided with a steam heating jacket.

If higher temperatures are necessary, heating coils must be used made either of electrically nonconductive materials, if available, or metals; these coils are directly immersed into the bath. When made of metals they must be prevented from functioning as bipolar electrodes; therefore special nonconductive protecting walls are placed between the coils and the electrodes, or the coils are conductively connected to one electrode.

To cool the electrolyte, either glass coolers or hollow ceramic tiles, made of stoneware having a good thermal conductivity, which cooling water flows through are convenient to use (e.g. Swiss "embrachit tiles" contain an addition of carborundum); sometimes coils with cooling brine are used. Direct cooling of the electrodes is very efficient but seldom employed (the electrodes are then formed as hollow rods or tiles). For less intensive cooling it is sufficient if the electrolyte flows through a cascade of electrolytic cells and vessels cooled by coils which are alternately placed between the adjacent cells.

IX. SOURCES OF DIRECT CURRENT

To accomplish the electrolytic process direct current is required. In the early stages of development of the electrochemical industry this sort of current was directly generated in D. C. generators; their capacity, however, was limited (20 000 A and 600 V was the attainable maximum) and their operation uneconomical; that is why at present direct current is produced exclusively by rectification of alternating current. Alternating current of a high voltage is generally led to the place of consumption where it is transformed first to the desired lower voltage and then rectified by a motor-generator set or by a synchronous converter (also called single phase rectifier) or by other types of rectifiers.

The motor-generator set comprises two machines on a common shaft, i. e. the motor and the generator. The motor is driven by alternating current whereby the electric energy is converted to mechanical energy; the latter is then transmitted by the common shaft to the generator where it is reconverted into electric energy in the form of direct current. The motor-generator set is less efficient than the synchronous convertor or mercury-arc or contact rectifiers because losses are encountered in both machines of the set (iron losses, copper losses and friction losses). If the motor has a full-load efficiency of 93 p. c. and the generator 95 p. c. then the efficiency of the whole rectifying set equals $0{,}93 \times 75 = 88.4$ p. c. With a half-load output the value of efficiency drops to some 70 p. c. Apart from this, the maintenance cost of such plant is comparatively high. On the other hand, they have an important advantage as the voltage of the motor generator set can be regulated by excitation almost within the entire range of output (up to the remanence); the set also withstands overloading to a satisfactory degree.

There are also generators designed for a direct connection to the electrical supply line of a higher voltage (e. g. 6000 V). If in this case a synchronous motor is used as the driving unit instead of asynchronous one, the motor-generator set can be used to correct the power factor of the electric supply line. In spite of these advantages motor-generators are only used today with small electrolytical installations (such as electroplating plants) where the lower efficiency does not bring about great economical losses as would be the case with large-scale installations.

The synchronous converter unlike the motor-generator set effects a direct rectification of alternating current without intermediate conversion of electric energy to mechanical energy. Conversion takes place in a machine which is fitted with one ring collector and three brushes to feed-in alternating current and one commutator with two brushes which take off the direct current. The voltage of both alternating and direct current in a synchronous converter are not so mutually independent as in the case of the motor-generator

set, but interdependent according to an exact relation, so that a stepdown transformer has to be inserted between the supply line and convertor terminals to reduce the primary voltage to a suitable value with regard to the required voltage of direct current. Also the voltage control is more difficult than in the case of a motor generator set.The choking coil connected to the side of alternating current just makes possible a 10 per cent regulation of the rated voltage. A wider range of control, but still only 50 p. c., can be attained by using a regulating three phase supply transformer. The advantage of the synchronous converter is mainly its higher efficiency, some 92 p. c. at full-load. Also less floor space is required as well as lower first cost. That is why quite a number of these machines were used in electrochemical industry during the period 1910 to 1930. However, they have been replaced by mercury arc rectifiers in modern electrochemical industry.

Rectifiers without moving parts are: aluminium or tantalum rectifiers, vacuum tube rectifiers, contact rectifiers and mercury-arc rectifiers. The first two types of rectifiers, the function of which has already been described in the theoretical section of this book are suitable for laboratory purposes only. Likewise vacuum tube rectifiers can also be used where a medium output is required; these tubes act as valves allowing the alternating current to pass through in one direction only; they are built for both low (up to 100 V) and high voltage (up to 10 000 V).

The copper oxide rectifiers and the selenium rectifiers belong to contact rectifiers (dry plate rectifiers). The key part of the copper oxide rectifier is a copper disc coated on one side with a thin layer of cuprous oxide; to achieve good contact a thin lead, aluminium or graphite disc is pressed against the oxide layer. The elements assembled in this way are inserted between cooling copper plates and copper washers to achieve a good dissipation of heat. The valve action of the element is best at between 0.7 to 3.0 V. If a higher voltage is to be rectified more units are clamped together and the supply of current is connected to the terminal plates. If stronger currents are required (up to 12 000 A) several such batteries of elements are connected in parallel. The selenium rectifier is based on the same principle, its element consists of an iron plate coated with selenium which is further coated with a suitable metal, for example cadmium. The alternating current passes through such a system in one direction only (from cuprous oxide into copper or from selenium into iron) whereby rectification is effected. Regulating transformers are the best means of controlling the voltage of contact rectifiers. The efficiency reaches the maximum values of 80 to 86 per cent. The advantage of these rectifiers is small floor space and minimum attendance.

For large electrochemical installations mercury-arc rectifiers are used which have proved valuable whereever strong direct current and relatively high voltage is required (above 300 V). In this case there is a loss of energy which is in proportion to the voltage necessary to overcome the arc resistance (20 to 30 V). As this voltage depends neither on the current nor on the total output

of the rectifier the efficiency is better the higher the operating voltage. According to this a rectifier operating at 50 V has an efficiency $100 \times 25/50 = 50\ \%$, at 400 V already $100 \times 375/400 = 93.7\ \%$ and at an operating voltage of 600 V the efficiency reaches 95.8 %. A great advantage of mercury arc rectifier lies in the fact that there are no moving parts (apart from the drive of the vacuum pump); therefore, supervisions do not have to be as careful as in case of the rectifying equipments with rotating parts. As the relation between the voltage of alternating current and direct current is constant a series transformer, generally a regulating type, is placed in the primary circuit to obtain direct current of the required voltage.

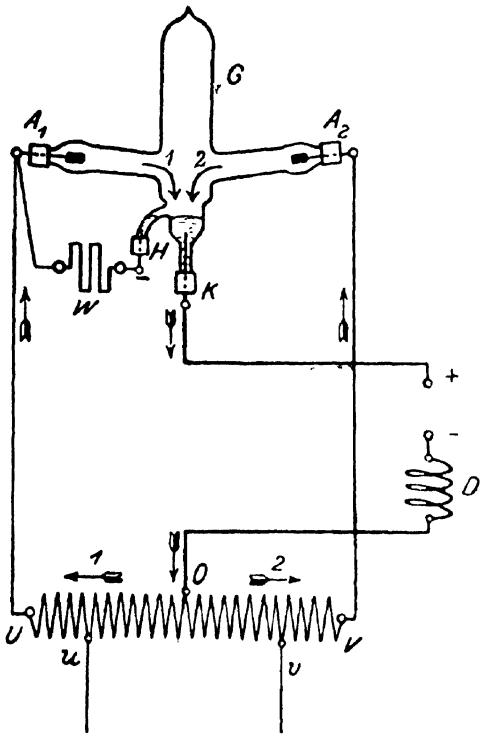


Fig. 55. Schematic diagram of a single phase mercury-arc rectifier

G — Single-phase mercury-arc rectifier, A_1 A_2 — Anodes, *K* — Cathode, *u*, *v* — Alternating current input, +, — — Direct current output, *D* — Choking coil, *W* — Resistance.

Mercury arc rectifiers are based on the electric valve action of the electrical discharge i. e. of an arc which is formed between the glowing mercury cathode and the cooled iron or graphite anode in the mercury vapour atmosphere inside the evacuated bulb. During the arc discharge a bright spot (of a temperature of some 2500 °C) moves on the surface of the pool of mercury (cathode) from which the electrons are emitted. These electrons collide with atoms of mercury vapour inside the bulb and in doing so ionize the mercury atoms (i. e. the mercury atoms are splitted to electrons and positive ions). The impact of these ions on the surface of the mercury cathode increases the temperature of the bright spot. The electrons liberated by ionization then proceed towards the cathode thus making possible the flow of current in oposite direction to the movement of electrons. The current flows only from the anode to the cathode and not in the opposite direction.

Fig. 55 is a schematic diagram of a single-phase mercury-arc rectifier fed from an autotransformer the terminals of which are marked *u* and *v* on the

primary side and U and V on the secondary side. In order to make use of both halves of the alternating current cycles rectifier G is fitted with two anodes A_1, and A_2, which are connected to the terminals of the autotransformer on the secondary side. Direct current is lead away from the cathode K and from the centre of the autotransformer. The voltage of the alternating current periodically maintains the positive potential of either anode so that the rectified "conventional" current always flows towards the cathode ($A_1 \rightarrow K$ and $A_2 \rightarrow K$ in repeated successions). Current fluctuations are damped by means of choking coil D connected in series. The rectifier starts operating by means of auxiliary electrode H which is connected to anode A_1 over the resistance W. When the rectifier is started it must be tilted so that the two pools of mercury accumulated at H and K merge into one. On restoring the rectifier to its normal position the pool of mercury is divided once again in two parts and gives rise to an electrical spark at the point of interruption; the heat evolved by the spark causes that a certain amount of mercury, sufficient to ignite the arc, evaporates.

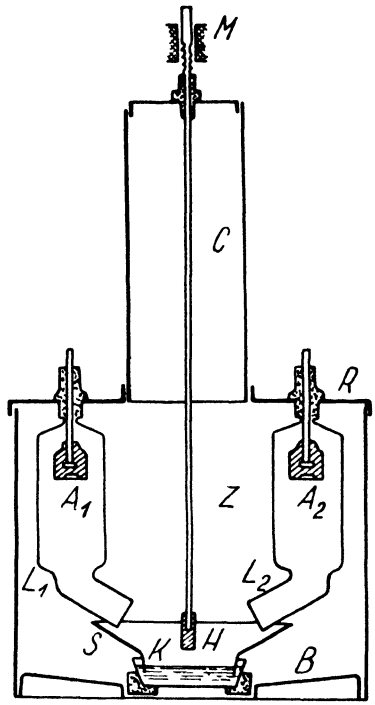


Fig. 56. Metal chamber mercury-arc rectifier.
A_1, A. — Anodes (six), K — Cathode, H — Needle igniter, C — Condensation cylinder, M — Electromagnetic breaking off of the ignition needle.

Large rectifiers (Figs. 56 and 57) for the rectification of three-phase currents are enclosed in metal chamber Z with a flat dish containing mercury K placed on the bottom of it. On the top of the chamber there is a cylindrical extension C which is cooled in order to effect condensation of mercury vapour. Six iron anodes A (there may be twelve or even eighteen of them) are suspended from ring R which covers the top of the chamber. Current for the rectifier is supplied by a three-phase transformer the secondary windings of which have their middles connected in a neutral point; in this way the secondary windings have six ends connected to six anodes A by choking coils D in series.

The arc is ignited by means of an ignition needle which carries auxiliary anode H; at first this is electromagnetically drawn into the mercury-filled dish; then the contact is interrupted which gives rise to an arc which spreads quickly to anodes A. The necessary vacuum in the tubes, some 0.001 millimeters of mercury column (apart from the partial pressure of mercury vapour) is maintained by a diffusion vacuum pump compounded with an oil type rotary vacuum pump.

Similar principles are used in the construction of the Ignitron rectifier which is very popular in the USA but not in Europe. It has the advantage of a lower arc voltage amounting to merely 15 V.

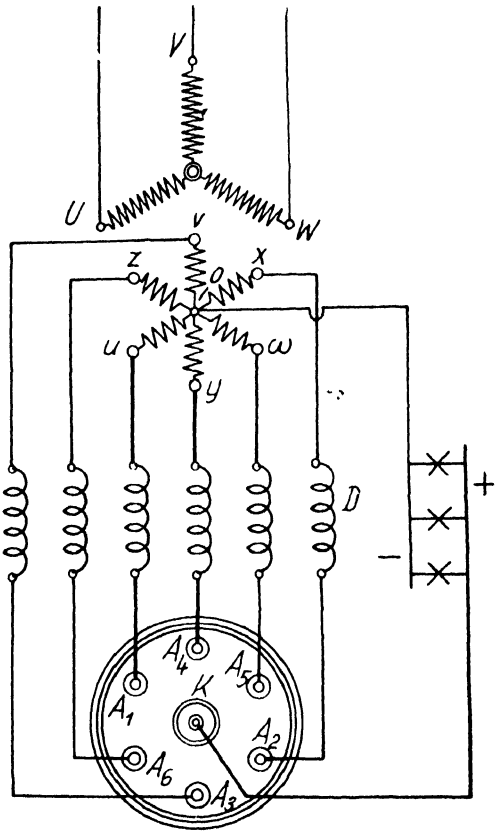


Fig. 57. Wiring diagram of a large mercury-arc rectifier.

U, V, W — Primary transformer windings. *u, z, v, x, w, y* — Secondary transformerwindings connected to six anodes (A_1 — A_6) of the rectifier.

When mercury-arc rectifiers were first introduced into industry some time ago many difficulties arose due to so called backfiring; this phenomenon is caused by one anode suddenly starting to work as a cathode and so giving rise to a double short circuit. This was overcome by taking meticulous care to see that the anode material was kept free of any impurities capable of emitting electrons.

Since 1939, industrial practice, i. e. the applied electrochemistry makes use of a mechanical device which converts alternating current into direct current; such devices are called mechanical rectifiers. These have mechanically controlled contacts which switch on and off according to the frequency of the alternating current so that they connect the phases at their highest voltage in cyclical sequence to the load system, thus converting the phase current to direct current. As the change of contact from one phase to another takes place at the very moment when the decreasing current attains zero value, the breaking of contact does not cause sparking which would impair the proper function of the device. The time interval during which the current of a phase has zero value is very short but it can be artificially prolonged if necessary to a sufficient length of time for effecting a sparkless break of contact by the use of a special choking coil.

This coil is, in principle, a ring-shaped core with toroidal winding. It is made of an alloy of nickel and iron (in approximate proportions of 1 : 1) which is characterized by a nearly rectangular hysteresis loop. The alloy is cold rolled

to a sheet of about 1 millimeter thickness, shaped so as to form a ring. This ring shaped magnetic core has very low self-induction resistance at strong currents yet very high self-induction resistance at weak currents. The change of the induction resistance takes place abruptly on transition of the core from a magnetically saturated state to a magnetically unsaturated state. Therefore in a mechanical rectifier with each contact connected in series with a reactance (choking) coil when a phase is near zero point the current is so weak that the disconnection can be effectuated at practically zero current and zero voltage, thus without sparking. The most sensitive parts of the rectifier are the contacts which are made of silver.

Smaller mechanical rectifiers of the six-phase type are built for a load of 5000 A with an efficiency approximating 95 per cent. In industry medium output units of twelve-phase type, built for a load of 10 000 A, having an efficiency of 98,8 per cent are used, or large units with 18 or even 24 phases and an efficiency practically equalling one.

On comparing the different kinds of rectifiers taking into account the first costs and energy losses, it may be stated that for plants using constant current up to 150 V, motor-generators or contact rectifiers prove most economical. Within the range of from 150 to 300 V there is competition between mechanical rectifiers and motor-generators while at voltages between 300 and 600 V mercury-arc rectifiers and mechanical rectifiers can be considered almost equally advantageous. If the voltage exceeds 600 V the mercury-arc rectifier proves the most economical as its efficiency under these conditions is fairly high. On the other hand, as an unduly high voltage entails a greater risk of accidents to the operator and a greater possibility of total current losses, there is a tendency in industrial electrochemistry to change over to electrolytic units which work with very strong current but without unduly high voltage (not exceeding 400 V).

X. ELECTROLYSIS OF WATER

When water is electrolytically decomposed, hydrogen and oxygen are generated. Both gases possess no taste, smell or colour. Hydrogen is 14.38 time lighter than air. At 0 °C and a pressure of 760 mm Hg 1 litre of pure dry gas has a weight of 0.089947 grams. It has a critical temperature of — 239.9 °C and a critical pressure of 12.8 atm. On being cooled below its critical temperature it can be liquefied to a liquid, boiling at — 252.7 °C, the lightest of all liquids known. If liquid hydrogen is allowed to boil at a pressure of some 50 mm Hg it solidifies into a colourless crystalline substance having a melting point — 259 °C.

Oxygen is 15.88 times heavier than hydrogen; 1 litre of the gas has a weight of 1.42893 grams at 0 °C and 760 mm Hg. It is rather easily soluble in water (4 volumes of oxygen dissolve in 100 volumes of water at 0 °C and 760 mm Hg). It has a critical temperature of — 118.8 °C and a critical pressure of 49.7 atm. Liquefied oxygen is a liquid of slightly bluish colour, boiling at — 183.0 °C at 760 mm Hg. On being cooled to — 219 °C it solidifies forming hexagonal slightly bluish crystals.

On burning hydrogen with oxygen to form liquid water H_2O (l) or water vapour $H_2O(g)$ at 25 °C (298. 1 °K) and 1 atm. pressure a great amount of heat is evolved:

$$H_2 + \tfrac{1}{2}\,O_2 = H_2O_{(l)}; \qquad \Delta H^\circ_{298,1} = -68{,}3 \text{ kcal},$$
$$H_2 + \tfrac{1}{2}\,O_2 = H_2O_{(g)}; \qquad \Delta H^\circ_{298,1} = -57{,}8 \text{ kcal}.$$

A mixture of two volumes of hydrogen with one volume of oxygen is called detonating (oxyhydrogen) gas. The ignition temperature of this mixture is about 550 °C and depends to a great extent upon the humidity of the mixture. Mixtures of these two gases in other proportions are also explosive; likewise mixtures of hydrogen and air (ignition temperature about 770 °C), but the limits of explosibility are in this case narrower. The temperature of an hydrogen flame in air equals 1970 °C; a hydrogen flame in oxygen has a temperature of 2500 °C.

A. THEORETICAL PRINCIPLES OF ELECTROLYSIS

When water is electrically decomposed hydrogen is evolved at the cathode and oxygen at the anode. In order to increase the low specific electrical conductance of chemically pure water, suitable electrolytes which possess a higher decomposition voltage than mere water are dissolved in it. Sodium or potassium hydroxides are most suitable for this purpose; acids or salts which may corrode the electrolytical installation should be avoided.

On electrolyzing a diluted solution of sodium hydroxide the current is transferred to the anode by hydroxyl ions which are discharged on the anode

surface to form gaseous oxygen. The current is transferred to the cathode by sodium ions which are present in the solution in a much higher concentration than hydrogen ions but on the electrode hydrogen ions are discharged, in spite of their negligible concentration in the electrolyte, because their deposition potential is more positive than that of sodium ions. The reduction of hydrogen ions at the cathode may be expressed by equation:

$$2\,H^+ + 2e = H_2 \qquad \text{(X-1)}$$

As no new H^+ ions migrate towards the cathode there must occur a dissociation of water molecules:

$$2\,H_2O = 2\,H^+ + 2\,OH^-, \qquad \text{(X-2)}$$

Thus, for each molecule of hydrogen evolved two molecules of water are dissociated.

The process at the cathode is therefore the consequence of the two aforementioned partial processes the result of which is the reaction:

$$2\,H_2O + 2e = 2\,OH^- + H_2 \qquad \text{(X-3)}$$

The hydroxyl ions thus formed migrate towards the anode where the following reaction occurs:

$$2\,OH^- = H_2O + \tfrac{1}{2}\,O_2 + 2e, \qquad \text{(X-4)}$$

whereby the passage of a quantity of electricity equalling two faradays is associated with the formation of one mole of water and half a mole of oxygen. It will be seen that in the process of forming of 1 mole of H_2 and $\frac{1}{2}$ mole of O_2 two moles of H_2O will be consumed at the cathode and 1 mole of H_2O formed at the anode. If the catholyte and the anolyte are separated by a diaphragm a difference in concentrations of the two parts of the electrolyte appears because the anolyte becomes more diluted. This dilution is further increased by the transfer of sodium ions from the anolyte to the catholyte. The dilution is partially compensated for by diffusion of the electrolyte from the more concentrated solution into the more diluted solution whereby the concentration difference acquires a stationary value depending on the current passing through the electrolytic cell and the magnitude of the diffusion resistance of the diaphragm.

Under normal conditions 865 grams of water are theoretically required to produce one cubic metre of hydrogen and $\frac{1}{2}$ cubic metre oxygen. Actually consumption is greater than this because the hydrogen and the oxygen evolved contain some water vapour the quantity of which depends on the temperature at which electrolysis is accomplished. If the electrolyzer operates at a higher temperature, and gases pass through a cooler which allows the water vapour to condense, the quantity of the vapour remaining in the gases is determined by the temperature of the condenser.

Energy economy of water electrolysis can be assessed from the current

efficiency as well as from the ratio of the theoretical decomposition voltage to the operating voltage across the electrolytic cell. The product of both values indicates the energy efficiency from which it can be seen the amount of energy consumed in actual operation compared with theoretical consumption.

1. Current efficiency

According to Faraday's law an amount of electricity equal to 1 A.-hr. will decompose 0.336 grams of water liberating 0.419 litres H_2 and 0.209 litres O_2 (at 0 °C and 760 mm Hg, in a dry state) or 2390 A.-hr. are theoretically necessary to produce 1 cubic metre of H_2 and ½ cubic metre of O_2.

The electrolysis of water proceeds without any side reactions and also the current losses which are caused by dissipation and by the recombination of hydrogen and oxygen dissolved in water are low. The current efficiency at normal pressure is, therefore, very good, reaching about 99 per cent. If electrolysis is carried out at a higher pressure the current efficiency is somewhat lower, as more gas is dissolved in the electrolyte which causes an increased quantity of the recombined hydrogen and oxygen.

2. Voltage

The minimum voltage necessary for the decomposition of water coincides with the theoretical decomposition voltage $(E_R)_t$ which can be calculated by using formula (VII-5) (see in the theoretical part) from the reversible oxidation potential at the anode ($\varepsilon_{Pt,O_2\,|\,OH^-}$) and the reversible reduction potential at the cathode ($\pi_{OH^-\,|\,H_2,Pt}$):

$$(E_R)_t = -E'_{min} = -(\varepsilon_{Pt,\,O_2\,|\,OH^-} + \pi_{OH^-\,|\,H_2,\,Pt}). \qquad (X\text{-}5)$$

The reversible oxidation potential at the anode where process (X-4) takes place can be expressed according to the Nernst law by the equation:

$$\varepsilon_{Pt,\,O_2\,|\,OH^-} = \varepsilon^{\circ}_{Pt,\,O_2\,|\,OH^-} - \frac{RT}{2F}\ln\frac{p_{O_2}^{\frac{1}{2}}}{a_{OH^-}^2} = -0{,}401 - \frac{0{,}05915}{2}\log\frac{p_{O_2}^{\frac{1}{2}}}{a_{OH^-}^2} \qquad (X\text{-}6)$$

The second form of this equation is valid at a temperature of 25 °C. Similarly the reduction potential at the cathode where hydrogen is liberated according to the equation (X-3) may be calculated from the equation:

$$\pi_{OH^-\,|\,H_2,Pt} = \pi^{\circ}_{OH^-\,|\,H_2,Pt} - \frac{RT}{2F}\ln a_{OH^-}^2 p_{H_2} = -0{,}828 - \frac{0{,}05915}{2}\log a_{OH^-}^2 p_{H_2}. \qquad (X\text{-}7)$$

In this equation $\pi^{\circ}_{OH^-|H_2,Pt} = -0.828$*) stands for the standard reduction potential of the hydrogen electrode immersed in a solution of alkali hydroxide with activity $a_{OH^-} = 1$ at 25 °C and hydrogen pressure of 1 atm.

On substituting equations (X-6) and (X-7) into equation (X-5) we obtain:

$$(E_R)_t = 1.229 + \frac{0{,}05915}{2} \log p_{H_2} p_{O_2}^{\frac{1}{2}}. \qquad \text{(X-8)}$$

This determines the value of the reversible decomposition potential of water if hydrogen escapes into the atmosphere at a pressure of p_{H_2} and oxygen at a pressure of p_{O_2}. If both gases escape at the pressure $p_{H_2} = p_{O_2} = 1$ atm., then the theoretical decomposition potential of water at 25 °C is:

$$(E_R)_t = 1.229 \text{ V}. \qquad \text{(X-9)}$$

According to this, the evolution of hydrogen and oxygen should commence from any aqueous solution at 1.23 V voltage across the electrolytic cell if no substances with a decomposition voltage below 1.23 V are present (such as hydrogen iodide or bromide). The actual decomposition voltage is higher because of the irreversible nature of electrodes, mainly of the oxygen electrode, which manifests itself by overvoltage (ω_k on the cathode and ω_A on the anode). A visible evolution of gas bubbles commences at some 1.7 V, when using smooth platinum electrode.

During electrolysis, when a certain current is allowed to flow through the electrolytic cell, the terminal voltage exceeds the theoretical decomposition voltage not only by the value of the overvoltage (which in turn rises with increasing current density) but also by the potential difference necessary to overcome the ohmic resistance of the solution (IR). The total voltage across the electrolytic cell is further raised by the resistance of the diaphragm, the electric conductors and connections and also by concentration polarization. The latter losses in voltage are almost negligible and no special attention should be paid

*) The reversible reduction potential of a hydrogen electrode immersed into a solution with hydrogen ions activity a_{H^+} can be calculated according to the reaction $2H^+ + 2e = H_2$ from the equation:

$$\pi_{H^+|H_2,Pt} = \pi^{\circ}_{H^+|H_2,Pt} - \frac{RT}{2F} \ln \frac{a^2_{H^+}}{p_{H_2}}.$$

As $\pi^{\circ}_{H^+|H_2,Pt} = 0$, we obtain at 25 °C and hydrogen pressure $p_{H_2} = 1$ atm:

$$\pi_{H^+|H_2,Pt} = 0{,}05915 \log a_{H^+}.$$

If we take into account the ionic product of water $a_{H^+} \cdot a_{OH^-} = 10^{-14}$ this equation can be transformed in the following manner:

$$\pi_{OH^-|H_2,Pt} = 0{,}05915 \log 10^{-14} - 0{,}05915 \log a_{OH^-} = -0{,}828 - 0{,}05915 \log a_{OH^-},$$

whereupon for an electrolyte with activity of hydroxyl ions $a_{OH^-} = 1$ we obtain:

$$\pi_{OH^-|H_2,Pt} = -0{,}828 \text{ V}$$

to them. The resultant operating voltage across the bath is determined mainly by the following components:

$$E = (E_R)_t + \omega_A + \omega_K + IR. \qquad \text{(X-10)}$$

In this case the losses in voltage due to the resistance of the electrolyte cannot be calculated by the usual method i. e. from the specific resistance of the solution, the spacing of the electrodes and the area of their surfaces; this difficulty is caused by the presence of gas bubbles suspended in the solution; these bubbles decrease the actual cross section between the electrodes, i. e. the area covered by the lines of force, and consequently the resistance of the bath rises. The decrease of conductance of the electrolyte caused by suspended bubbles is more marked when the current is higher, the height of electrodes greater (as bubbles accumulate mainly at the upper end of the electrode), the electrolytic cell narrower and the movement of the electrolyte slower. The amount of bubbles in one unit of volume also depends on the viscosity and the temperature of the electrolyte.

3. Energy consumption

The theoretical consumption of electric energy necessary to produce 1 cu. m. of H_2 and ½ cu. m. of O_2 measured at 1 atm and 0 °C is determined by the equation:

$$W_t = (E_R)_t \, q_t \quad \text{kw-hr.} \qquad \text{(X-11)}$$

into which we in this case substitute 1.23 V for $(E_R)_t$ and 2.39 kA.-hr for q_t:

$$W_t = 1.23 \times 2.39 = 2.95 \text{ kw-hr.}$$

The actual consumption of energy exceeds the theoretical amount because the operating voltage varies from 1.9 to 2.6 V, depending on the design of the electrolytic cell. This entails a rise in energy consumption from 4.5 to 6.2 kw-hr. which corresponds to an energy efficiency of 65 to 48 per cent.

4. Heat evolution within electrolytic cells

As has been already mentioned the theoretical decomposition voltage of water equals 1.23 V while its practical value amounts to minimum 1.7 V and the actual operating voltage to 1.9 V. It would be erroneous to think that all the energy corresponding to the difference between the actual and the theoretical voltage across the electrolytic cell is converted into heat which warms up the electrolyte.

In the theoretical section of this book we learnt that the change in free energy encountered in a reversible reaction proceeding at a constant temperature can be expressed by the difference between the corresponding change in enthalpy ΔH and latent heat Q_{rev} which must be released by the system to the sur-

roundings or accepted from it in order to have an isothermal process (see equation VI-2).

This holds good for galvanic and electrolytic cells. In the case of electrolysis of water at 25 °C the following values have to be considered:

$$H_2O_{(l)} = H_2 + 1/2O_2;\ \Delta H_{298,1} = 68372 \text{ cal.}$$

and

$$\Delta G^\circ_{298,1} = 56693 \text{ cal.}$$

If we first use the equation (VII-4) which expresses the relation between the change in free energy and the theoretical decomposition voltage $(E_R)_t$, we obtain:

$$(E_R)_t = \frac{\Delta G^\circ}{23066\ n} = \frac{56693}{2 \times 23066} = 1.229 \text{ V.}$$

This value is in complete agreement with the result obtained on the basis of electrode potentials.

Latent heat can be calculated from known values of ΔH° and ΔG° using equation (VI-2):

$$Q_{rev} = \Delta H^\circ - \Delta G^\circ = 68372 - 56693 = 11679 \text{ cal}$$

It can be seen that the electrolytic cell must accept 11 679 cal. from the surroundings per each mole of decomposed water to keep a constant temperature (when working adiabatically the electrolytic cell would cool down). This heat is also covered by electric energy. Therefore, to achieve an isothermal decomposition of a mole of water a total amount of not only 56 693 cal. but 68 372 cal. in the form of electrical energy is necessary which corresponds to the minimum terminal voltage across the electrolytic cell:

$$(E'_R)_t = \frac{68\,372}{2 \cdot 23\,066} = 1.48 \text{ V.}$$

If an electrolytic cell operates with current I at terminal voltage E it accepts a total amount of $0.86\ EI$ kcal. per hour. A part of this energy equalling $0.86\ (E'_R)_t\ I = 0.86 \cdot 1.48\ I$ is consumed in the isothermal decomposition of water and the remnant Q_u is the heat liberated within the cell in the form of Joule's heat:

$$0.86\ EI = 0.86 \cdot 1.48\ I + Q_u,$$

thus

$$Q_u = 0.86I\ (E - 1.48) \text{ kcal/h.} \qquad \text{(X-12)}$$

According to this result, the heat generated within an electrolytic cell is proportional to both the current and the difference between the operating voltage and 1.48 V. It will be seen that the computed value of 1.48 V is not identical

with the theoretical decomposition voltage of 1.23 V or with the practical decomposition voltage of 1.7 V. In an exact calculation it is also necessary to take into account the quantity of electric energy consumed in the formation of vapour with which the liberated gases are saturated. Such an exact calculation shows, for example, that on electrolysis of a sodium hydroxide solution of 1.20 specific gravity at 80 °C (partial pressure of water vapour in gases being 280 mm Hg) only energy corresponding to a voltage above 1.65 V will be converted into heat and so warm the electrolyte to a temperature higher than that of the surrounding medium.

B. BASIC ELEMENTS IN THE DESIGN OF ELECTROLYTIC CELLS

Electrolytic cells should meet the following requirements: Minimum quantity of energy consumed, high purity of gases produced, easy operation, minimum space required, cheap maintenance, long service life and low first costs.

1. Types of electrolytic cells

Main types of electrolytic cells are shown in Figs. 58—62.

According to Fig. 58 both electrodes, *A* and *K* are placed in a closed container *G* and separated by diaphragm *D*. Fig. 59 represents a simple type where the opposite walls of the electrolytic cell act as anode and cathode; these walls are separated from other metallic parts of the electrolyzer by means of insulating packing *B*. In the electrolytic cell shown in Fig. 60 the separation of gases is

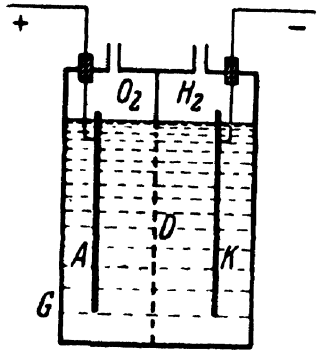


Fig. 58. Schematic diagram of an electrolytic cell for decomposition of water with electrodes separated by a diaphragm: *A* — Anode, *K* — Cathode, *G* — Electrolytic vessel, *D* — Diaphragm.

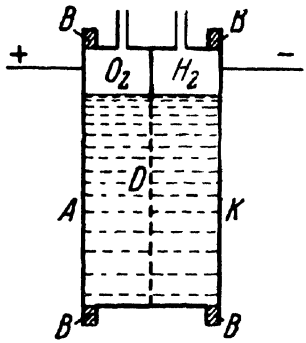


Fig. 59. Schematic diagram of an electrolytic cell with a diaphragm; the walls of the cell act as electrodes. *A* — Anode, *K* — Cathode, *D* — Diaphragm, *B* — Insulation.

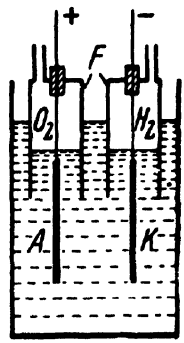


Fig. 60. Schematic diagram of an electrolytic bell-jar cell: *A* — Anode, *K* — Cathode, *F* — Bell-jar.

achieved by means of long narrow bell-jars traversed by insulated conductors which carry the current to anode A and cathode K. The connection in series of several monopolar electrodes represented in Fig. 59 in a common bath (see Fig. 61) is equivalent to a system of bipolar electrodes which act as cathodes on one side and as anodes on the other side (see Fig. 62). Bipolar electrodes are used in electrolytic cells of the tank type and the filter-press type.

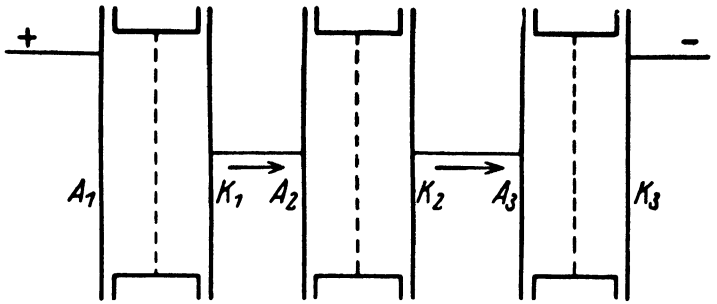


Fig. 61. Schematic diagram of several electrolytic cells connected in series: A — Anodes, K — Cathodes.

Generally, electrolytic cells with bipolar electrodes of the filter-press type are preferred for the electrolysis of water rather than electrolytic cells with monopolar electrodes. The advantage of the first type is that by assembling the requisite number of individual chambers into one block the terminal voltage across the electrolytic cells can be easily adjusted to the line voltage. For instance an installation for 500 kw and 250 V operating voltage can be carried out by one electrolyzer consisting of 125 individual chambers through which a current of 2000 A flows with a voltage across one chamber of 2 V. On the other hand if monopolar electrolyzers are used 125 individual cells, though smaller in size, would be needed to achieve the same result, unless cells for stronger current and lower resultant voltage were preferred. Large bipolar units are built for capacities up to 1000 kw (Pechkranz, Bamag) while the capacity of mono-

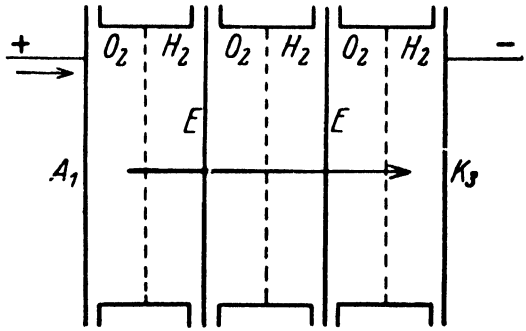


Fig. 62. Schematic diagram of electrolytic cells with bipolar electrodes: A — Anode, K — Cathode, E — Bipolar electrodes.

polar electrolyzers does not exceed 40—50 kw even with a current of 20 000 A. A disadvantage of the bipolar electrolyzers is the complicated packing and difficult access to the individual parts if repair is necessary.

The development of electrolyzers is a result of efforts made in order to reduce to a minimum the amount of energy needed for decomposing water. As the current efficiency is generally about 99 per cent, which is very satisfactory, designers first of all concentrated their efforts on reducing the operating voltage. This can be done in several ways. As overvoltage on electrodes rises with an increasing current density, the voltage and the amount of energy consumed can be reduced by enlarging the surface of the electrodes. To avoid any alternations in the external dimensions of the cell the surface of the electrodes is enlarged by assembling them from a great number of lamellae or narrow metal plates.

Energy consumption can also be reduced by lowering the overvoltage if suitable materials are used for the electrodes. Among the different and comparatively cheap materials are iron, nickel and nickel-plated iron most suitable. Cathodes are usually made of soft iron with a roughened surface to lower the overvoltage; anodes are made of iron electroplated with dull nickel. It is also advantageous if the electrodes are electroplated with a layer of nickel containing some nickel sulphide (Ni_2S_3) obtained by addition of thiosulphate to the nickel-plating bath; overvoltage on such electrodes is substantially lower than on the surface of pure nickel; a cathode prepared in this way acts in this respect very much like a platinized platinum electrode. Electrodes with electrolytically deposited layers of spongy nickel or iron are also recommended.

The temperature of the electrolyte is another factor which has a great influence on the amount of energy consumed; the higher the temperature, the lower the terminal voltage of the electrolytic cell at a given current density (this is due to lesser specific resistance of the solution and lower overvoltage). For this reason electrolysis is carried out at a temperature as high as possible but corrosion of the component parts of the electrolyzer and the great amount of vapour formed must also be taken into account; under these circumstances it is best to work at temperatures from 60 to 80 °C. The vessels of smaller units which work periodically are covered by an insulated jacket heated by hot air or vapour at the commencement of the operation. Larger vessels for continuous operation generate a considerable amount of heat and must be cooled by means of coils with cooling liquid flowing through them. In the case of a bipolar electrolyzer with an outer circulation of the electrolyte a cooler is connected into the circuit.

As already said neither acids nor salts are suitable for lowering the specific resistance of water because of their corrosive effect.*) Therefore only sodium or

*) In the case of sulphuric acid the equipment could be made of lead. But owing to the high decomposition voltage of water on this metal, 2.7 to 2.8 V, it is not practicable.

potassium hydroxide can be used as electrolyte (solution of sodium carbonate is less conductive than hydroxides). The conductance of potassium hydroxide is better than that of sodium hydroxide, especially at a lower temperature. Because of this, KOH is preferred to sodium hydroxide, although the latter is cheaper and not so corrosive.

The specific resistance of both hydroxides decreases with increasing concentration to a certan minimum which depends on the temperature. From this it can be deduced that the concentration of the electrolyte should correspond to the assumed temperature of the electrolyte, if the resistance of the bath is to

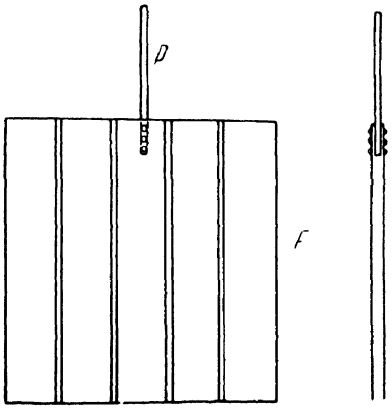


Fig. 63. Double plate electrode:
E — Electrode plate, *P* — Current conductor.

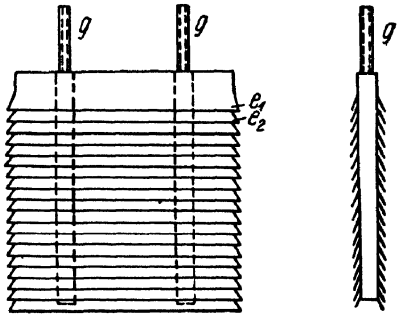


Fig. 64. Louvre type electrode:
g — Louvre supports, current conductor, e_1, e_2 — Louvres.

be kept as low as possible. Fortunately the course of the curve illustrating the relation between the specific resistance of the electrolyte and the concentration is fairly level in the vicinity of the minimum value of the resistance; therefore, no great mistake will be made if a less corrosive solution is used which is slightly more diluted than corresponds to the optimum conductance. In technical practice electrolytic cells working at 60—65 °C use potassium hydroxide with 25 to 29 per cent KOH, or sometimes sodium hydroxide with 16 to 18 per cent NaOH.

As already mentioned the resistance of the electrolyte does not only depenc on the specific resistance, the spacing and the surface of the electrodes, but also on the ratio of the volume of gas bubbles to the total volume of the electrolyte. The influence of bubbles upon conductance is considerable; for instance if the volume of bubbles in the electrolyte equals 35 per cent, resistance is twice that of an electrolyte without bubbles. If bubbles are present in the electrolyte the summary resistance across the electrolyte cannot be decreased by bringing the anode closer to the cathode, because the effect of the gas accumulated in this

smaller space more than counteracts the reduced distance between the electrodes (which would normally lower the ohmic resistance). The principle of many designs is, therefore, based on a quick removal of the liberated gases from the electrolyte by a suitable adaptation of the electrolytic cell. Sometimes, this problem is solved when the electrolyte between the anode and the cathode is set

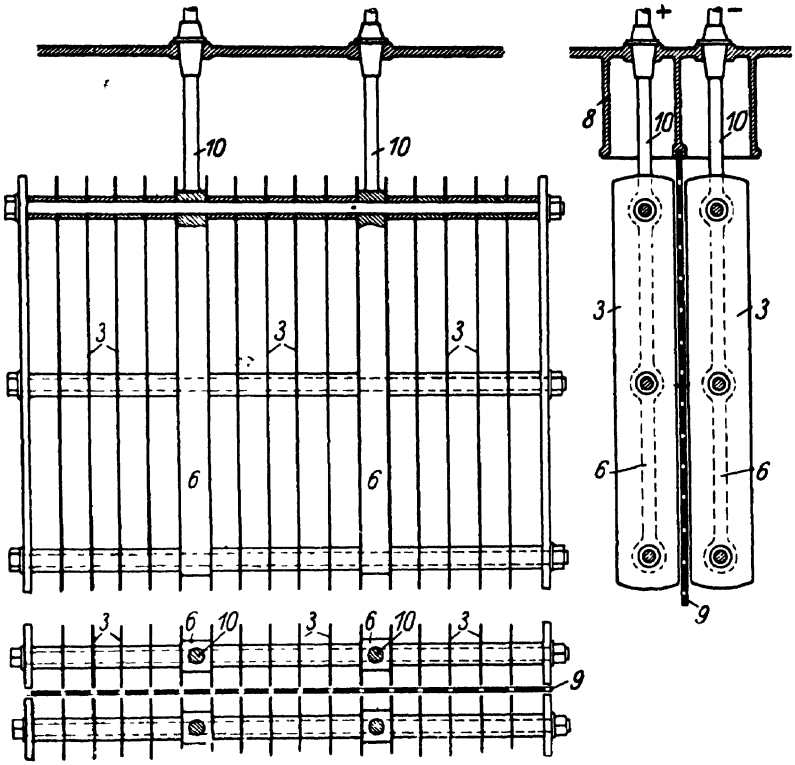


Fig. 65. Lamellar electrode:
3 — Individual lamellae, *6* and *10* — Current conductors, *8* — Part of the cover with gas collecting bells, *9* — Diaphragm.

into fairly quick motion; sometimes suitably divided electrodes are used which force the gases to find their way from the reaction space to the other side of the electrodes immediately after liberation. The use of pressure during the operation (see later) also reduces the undesirable influence of bubbles on the resistance of the electrolyte.

Electrodes are designed to meet the above requirements and accordingly various types of electrodes exist.

If single plate electrodes are used the motion of the electrolyte which is caused by the escaping gas bubbles is negligible in the close proximity of the electrodes; therefore many bubbles remain suspended in the electrolyte. In order to reduce the quantity of bubbles as much as possible, the height of the electrode should not exceed half the length; apart from this a low intensity of current is used, i. e. 2 to 3,5 A/sq. dm.

Double plate electrodes are more advantageous in this respect (see Fig. 63). They are assembled of two plates arranged parallel and reinforced by means of ribs the tops of which are connected to a common current conductor.

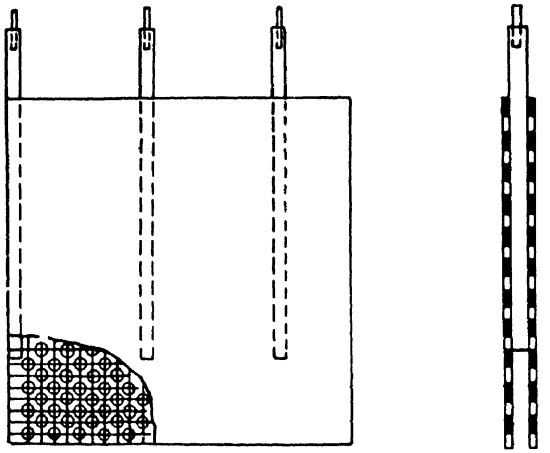


Fig. 66. Perforated plate electrode.

On electrolysis the gas is evolved only at the outer side; in the inner space between the plates the electrolyte without bubbles sinks to the bottom due to its higher specific gravity and is raised once again by gas bubbles evolved at the outer side. The electrolyte, after most of the gases have been separated, flows back into the space between both plates. Owing to this spontaneous circulation the quantity of gases remaining in the electrolyte is less than in the previous case which makes it possible to increase the current density to 4—5 A/sq. dm.

With the so called louvre type electrodes, is the electrode proper carried by two iron bars which at the same time conduct the current; welded to the bars on both sides are iron plates inclined at a certain angle with respect to the vertical line and arranged to form a sort of shutter or louvre (design *Casale*). The gas bubbles, after being evolved, rise on the individual plates and slide along the inclined lower surface of the plates lying immediately above into the inner space of the electrode wherefrom they then rise to the electrolyte surface into a small bell which is formed by the two top louvre plates (see Fig. 64). In the

arrangement described the major part of the gas is carried away from the area of the electrolysis proper which considerably increases the conductivity of the electrolyte. This arrangement and the increased area of the electrode permit an increase in current density approximately to 20 A/sq. dm of the orthogonal projection of the electrode area. The disadvantage of the louvre type electrodes

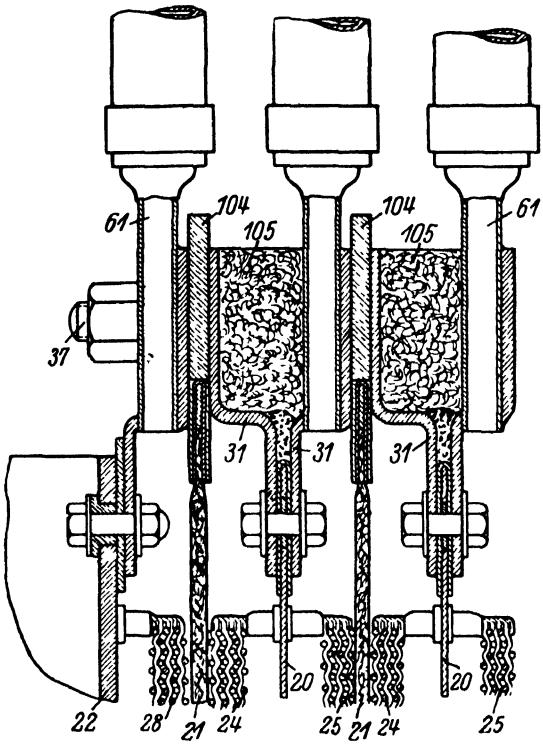


Fig. 67. Bipolar electrolyzer with extended electrodes.

20 — Middle plates bolted to the frames *31*, *21* — Diaphragms, *22* — Front plate of the electrolyzer *24*, *25*, *28* — Extended electrodes, formed by several layers of wire gauze, *31* — Frames, *37* - - Clamping bolts, *61* — Gas and electrolyte outlet, *104* — Insulation packing, *105* — Thermal insulation.

is their complicated design and insufficient purity of both gases because their separation at higher current densities is in large units by far not perfect.

With lamellar electrodes the main idea is to decrease the voltage across the bath by increasing the electrode surface area. To this a great number of lamellae are used, held in position by spacers; the whole set is then tightened together by horizontal clamping bolts. The electrode bundles so formed are inserted into the electrolyzer in such a manner so that the individual plates are

set at right angles to the diaphragm. In this arrangement are the electrodes carrying opposite charges not facing each other. The lines of force, therefore, do not penetrate evenly in the inner space between the individual lamellae so that a part of their area will not be utilized. Nevertheless this design increases the electrode area many times in comparison with the orthogonal projection of a simple electrode. Figure 65 shows such design where *3* marks the individual lamellae or plates, *6* and *10* the current conductors, *8* part of the cover with the gas collecting bells and *9* the diaphragm. The increased surface area of the lamellar electrodes enables work to be carried out with a current density up to 15 A/sq. dm of their orthogonal projection.

From the point of view of a simple design perforated plate electrodes are of advantage, as the lower operating voltage is obtained with them because the gases are quickly carried away from the region of electrolysis. Such an electrode is formed by two parallel iron plates with a large number of round perforations through which a considerable amount of gases will pass to the inner part of the electrode and so will be removed from the region of the electrolysis proper. The perforated plates are welded to two iron bars which carry the electrodes and to which the current supply is connected (see Fig. 66).

Instead of a perforated plate electrode a wire gauze could be used and by placing the electrodes closely to the dividing asbestos diaphragm the gases would be driven from the space between the anode and cathode. Such a design of bipolar electrodes tightly bolted together to form a filter press is illustrated in Fig. 67. Here *20* marks the middle plates bolted to the frames *31*, *22* the front plate of the filter press electrolyzer, *24*, *25* and *28* the extended electrodes formed by several layers of wire gauze, *21* the diaphragms, *104* the insulation packing, *61* the gas outlet from the electrolyzer, *105* the thermal insulation and *37* the bolts by which the electrolyzer is clamped together. The outlet of gases into the space behind the electrodes, the electrolyte circulation and especially the close spacing of the electrodes permit the application of current density up to 25 A per sq. dm. of the orthogonal projection of the electrode.

2. Separation, cooling and washing of gases

In order to obtain as far as possible pure hydrogen and oxygen and to prevent the possible formation of detonating gas, both gases must be separated. The simplest way of doing this is the immersion of iron bells in the electrolyte; the gases are carried away from the bells via side tube and the electrodes protected by an insulator pass through the centre of the cover of the bells (see Fig. 60).

For a satisfactory separation of gases it is more advantageous to use a diaphragm, because the bells occupy too much space and increase the distance and the resistance of the electrolyte between the electrodes. In this case the diaphragm should not prevent the diffusion of the dissolved substances in the anolyte, or in catholyte but only prevent the mixing of the evolved gases; in fact the greatest possible diffusion is very beneficial for the suppression of

concentration polarization. The separation of the anolyte and catholyte by means of a diaphragm can be carried out as illustrated in Fig. 58, or it can be combined with the bells so that an asbestos diaphragm will be suspended from one or both bells. The diaphragm forms a bag which entirely envelops the electrode. The bells may be quite short and narrow so that the electrodes can be closely spaced together.

In the course of operation care must be taken to keep the level of the electrolyte in the electrolyzer above the lower edges of the bell in order to prevent the diaphragm emerging from the electrolyte and cause an easy diffusion of the gases.

Pure, long-fibre asbestos without any organic admixtures will best meet the requirement of good diaphragm (i. e. resistance against the electrolyte, good mechanical strength, sufficient thickness to prevent the permeation of bubbles and low electric resistance). The diaphragm is woven of asbestos yarn 1.5 to 3.5 mm thick. The asbestos diaphragm will last some years (3 or more), especially if freely suspended in the electrolyte and not attached to a frame, in which case it would be exposed to mechanical stresses caused by the uneven pressure of the hydrogen and oxygen. To increase its mechanical strength the asbestos cloth is sometimes interwoven with nickel wire.

A metallic diaphragm, made of nickel foil with great many perforations (800 to 1400 to 1 sq. cm), prepared in an electrochemical way is used with some electrolyzers (Pechkranz). A metallic diaphragm behaves as a nonconductor in the cell because the current meets with a lower resistance in the course of flowing through the electrolyte within the perforations than flowing through metal and having to overcome not only the ohmic, but also polarization resistance as well, at the interface between the solution and the diaphragm. When using metallic diaphragms it is absolutely essential to prevent any contact with the electrodes because a metallic diaphragm will also act as an electrode and contaminate the gas at the other electrode. Therefore, the electrodes must not be placed too closely together.

The gases leave the electrolyzer at a temperature of 60 to 80 °C and contain vapour and fine droplets of the electrolyte entrained in the form of fine mist. In order to condense the vapour and to separate the electrolyte the gases are cooled in the collecting bells and by bubbling through a layer of cold feeding water in gas washers. By a suitable connection of washers automatic compensation of the gas pressure in the hydrogen and oxygen compartment can be carried out at the same time. The regulation of the gas pressure is of great importance as an uneven taking off of one of the gases or clogging of the pipes may cause a lowering of the electrolyte level below the lower edge of the collecting bell which would expose the diaphragm. This in turn would lead to the formation of detonating gas. An uneven gas pressure will also cause a mechanical stress in the diaphragm which would result in a reduced service life of the diaphragm.

The electrolyte level must be kept constant by distilled water refilling. The

water feed in large installations is automatic. Water is fed to the electrolyzer from a pressure tank by means of a valve automatically controlled by a float type controller. Pressure controllers are more advantageous for enclosed electrolyzers.

For electrolyzer feeding only distilled or electro-osmotically purified water is used which may contain only 7 mg of solid residue from evaporation per litre and have a minimum specific resistance of 60 000 ohm. cm.

C. TYPES OF INDUSTRIAL ELECTROLYZERS

Industrial electrolyzers can be divided, according to the manner in which the electrodes are connected and to the type of electrode, as follows:

Monopolar electrolyzers

Electrolyzers with single plate electrodes.
Electrolyzers with double plate electrodes (open or closed).
Electrolyzers with louvre type, lamellar, or perforated electrodes.

Bipolar electrolyzers

Tank electrolyzers.
Filter press electrolyzers with single plate electrodes.
Filter press electrolyzers with extended electrodes.

1. Electrolyzers with monopolar electrodes

An example of an electrolyzer with single plate electrodes is the old *Knowles* design. Thin nickel-plated iron plates are connected alternately to the positive and negative pole of the current source and suspended parallel in an open iron tank. The gas collecting bells are over the electrodes. From the hydrogen collecting bells asbestos diaphragms are suspended to prevent the gas mixing. Hydrogen and oxygen is first led to a gas collecting pipe; from there the gases flow to a corrugated and air cooled gas main to which more tanks are connected. Here the water is condensed and flows back to the electrolyzer. Next the gas is led into two washing and separating tanks, where the droplets of the electrolyte entrained are removed. These tanks are also used to control the quantity of the distilled water feeding. About 20% sodium hydroxide solution is used as electrolyte which in open tanks will be carbonized after a certain period so that it will have to be replaced. These electrolyzers are built for currents of 166 to 10 000 A upon which the size and number of electrodes depend. An electrolytic tank for a current load of 10 000 A is approximately 1300 mm long, 2400 mm wide and 1300 mm high and contains 41 electrodes. This electrolyzer operates with a maximum current density of about 3.5 A/sq. dm. at a normal voltage

of 2.25 V. The corresponding power consumption is 5.4 kw-hr. per 1 cu. m of H_2 and 0.5 cu. m of O_2 (at 0 °C and 760 mm Hg). The hydrogen produced is 99.5% pure and the oxygen 99.0 %. When increasing the load to 15 000 A, the voltage rises to 2.5 V (with a proportionate rise in power consumption). During electrolysis the electrolyte temperature is kept at 60 °C, at higher loads the electrolyte

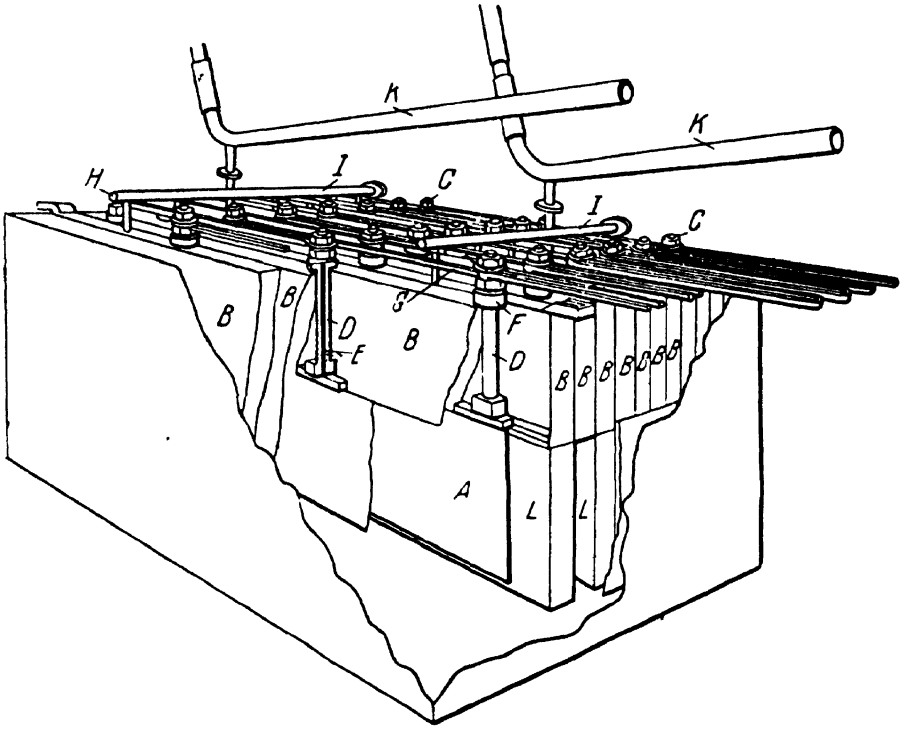


Fig. 68. Arrangement of the Knowles electrolyzer.
A — Nickel plated, iron electrodes, *B* — Gas collecting bells, *C* — Current supply, *D* — Current conductors to the electrodes, *E* — Insulation pipe, *G, H* — Current conductors, *I* — Gas collecting pipe from the individual bells, *K* — Gas pipe, *L* — Asbestos diaphragm.

is cooled by means of inserted cooling coils. The Knowles electrolyzer is illustrated in Fig. 68.

In an electrolyzer with double plate electrodes (design *Fauser*) each electrode is composed of two parallel plates (the anodes are nickel-plated) suspended by bolt *V* in the dome *N* or *U*, situated over the gas collecting bell *G* (see Fig. 69). From each bell hangs the diaphragm *H*, made as a narrow long bag which can be closed or opened at the bottom. The current is conducted to each electrode by nickel-plated copper strips *P*. The hydrogen collected in the dome *N* flows

through the holes *S* to the collecting bell *M* which serves all the hydrogen domes of the electrolyzer and its bottom edge is immersed into the electrolyte. Analogously oxygen is drawn off from dome *U*. The electrolyzers are fed with water from a common pressure tank by a float type controller. The temperature of the electrolyte is kept at 60 to 70 °C; in large installations the external walls of the electrolytic tank are sprayed with water. The *Fauser* electrolyzer is designed

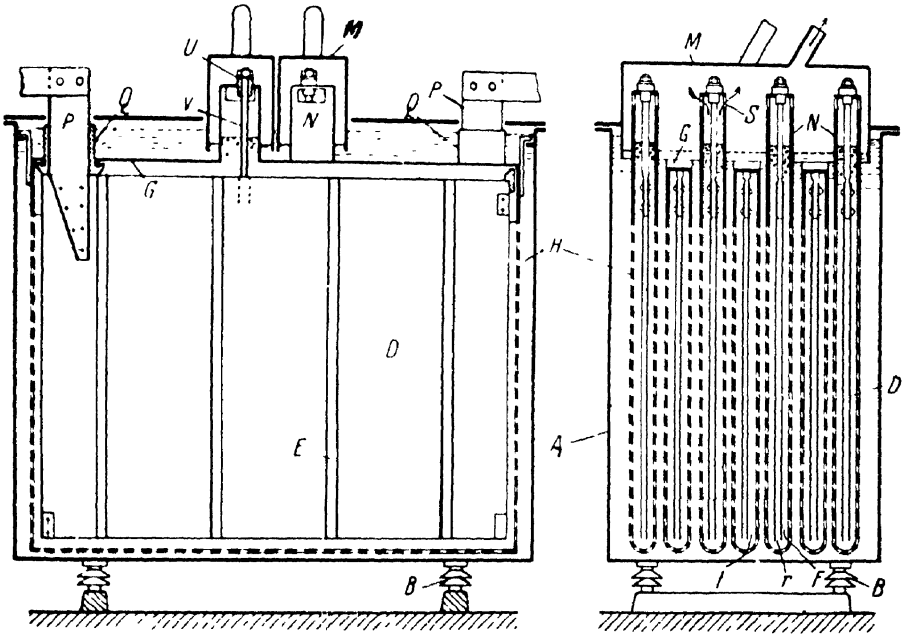


Fig. 69. Fauser electrolyzer.

A — Tank, *B* — Insulators, *D* — Double plate electrodes, *E* — Reinforcement of the electrode plates, *G* — Gas collecting bell, *H* — Diaphragm, *M* — Collecting bell, *N* — Hydrogen dome, *P* — Nickel-plated copper strips (current conductors), *S* — Holes in the dome, *U* — Oxygen dome, *V* — Bolts for suspension of the electrodes in the domes.

for currents of 6000 to 14 000 A and is more compact than the Knowles type. Because the electrodes used here increase the electrolyte circulation and hence a quick removal of the gas bubbles, electrodes of double height can be used at a current density up to 4—5 A/sq. dm. The terminal voltage ranges from 2.1 to 2.3 V. The electrolyzer is of open design so that the electrolyte after a certain time becomes carbonized owing to absorption of atmospheric carbon dioxide which decreases conductivity. Therefore, the carbonized solution has to be replaced from time to time by a fresh solution. The electrolyzer is sometimes closed by a cover to prolong the life of the electrolyte. The electrode plates are then

placed more closely together and openings are made in the upper part to enable the electrolyte to circulate. This arrangement allows to increase the current density up to 6 A/sq. dm without increasing the voltage, necessary to overcome the total resistance of the electrolyte, above 2.05 V. Under these conditions the electrolyte temperature will not rise unduly so that the electrolyzer does not need any additional cooling.

Casale when designing his electrolyzer endeavoured to separate the gases by means of the louvre type electrodes without the application of diaphragm. In

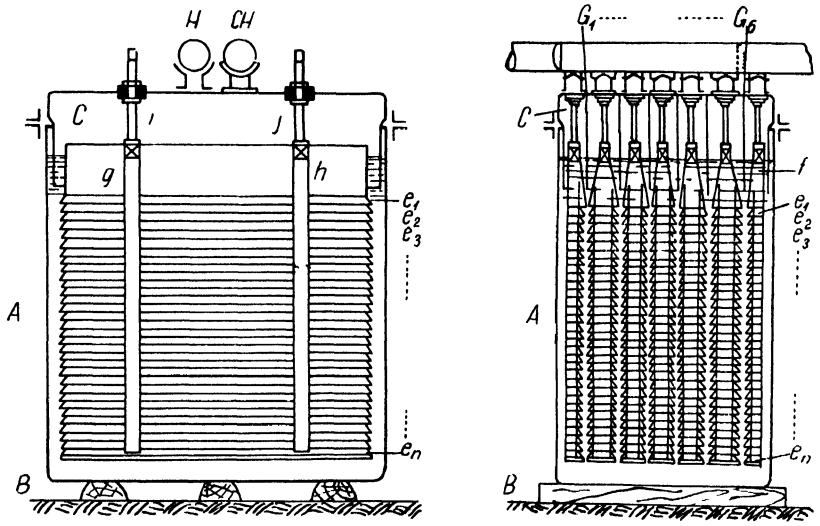


Fig. 70. Casale electrolyzer.
A — Electrolyzer tank, *B* — Insulation plates, *C* — Gastight cover, e_1, e_2 — Electrode elements (louvres), *G* — Partitions, *H*, *CH* — outlet of separated gases (H_2, O_2).

this way the gases evolved from the space between the electrodes would be led to the rear and from there to the gas collecting bells and to the collecting pipes. In fact the desired gas separation was accomplished in small units only; in large electrolyzers pressure variations result in a partial mixing of both gases. In later design an asbestos cloth diaphragm suspended from the edges of the collecting bells was used to facilitate the required separation of both gases (see Fig. 70).

Electrolyzers provided with lamellar electrodes (design *Holmboe*) give better results than electrolyzers with louvre type electrodes. They are composed of a great number of vertical lamellae fastened by bolts *2* at right angles to the diaphragm which increases the surface area. Electrolyzer tank *3* closed by a cover *4* is provided with inside partitions to receive the hydrogen collecting

bells on which the asbestos diaphragm hang. The diaphragms surround the lamellar cathodes *1* which are fastened by insulated hangers *5* to the cover and connected to the negative current conductor *8*. Anodes *6* are not provided with diaphragms but are screwed by means of clamping bolts *7* to the electrolyzer tank to which the positive current conductor is connected. The hydrogen is drawn off from the gas collecting bells, interconnected by channels *10*, and the oxygen from the space between the collecting bells (see Fig. 71).

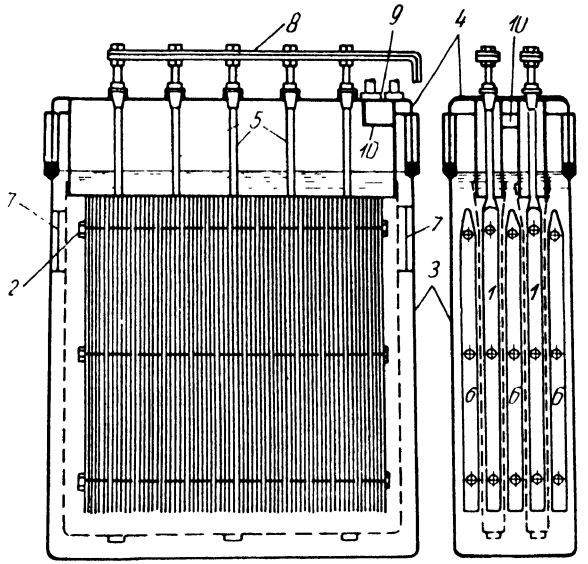


Fig. 71. Holmboe electrolyzer with lamellar electrodes.

1 — Lamellar cathodes, *2* — Bolts clamping the electrode lamellae, *3* — Electrolyzer tank *4* — Cover, *5* — Insulated cathode hangers, *6* — Lamellar anodes, *7* — Clamps for fastening the anodes directly to the tank, *8* — Conductor from the negative pole of the current source, *9* — Conductor from the positive pole of the current source, *10* — Channel interconnecting the hydrogen collecting bells.

Those electrolyzers are built for currents of up to 18 000 A and produce 99.5 to 99.9% hydrogen and 99.5% oxygen. At an average current load of 10 000 A, voltage across the electrodes is approximately 2.2 V. The electrolyzers are usually connected in a series of 250 to 350 electrolyzer tanks to the direct current source with a voltage of 500 to 700 V.

A special type of electrolyzer with perforated double plate electrodes was designed in the USSR for the current load of 14 000 A (electrolyzer type V — 3). This electrolyzer tank is covered by a cover from which 10 anodes and 11 cathodes formed by perforated iron plates are alternately suspended (see Fig. 72).

The top ends of the anodes pass through collecting bells *15* which are welded to the cover and carry the asbestos diaphragms. The oxygen flows from the collecting bells into collecting pipe *2* and the hydrogen from the space between the bells to pipe *3*. The 70 °C hot and humid gases are cooled and washed in two cooling columns *4* connected in parallel. During this stage the gases enter

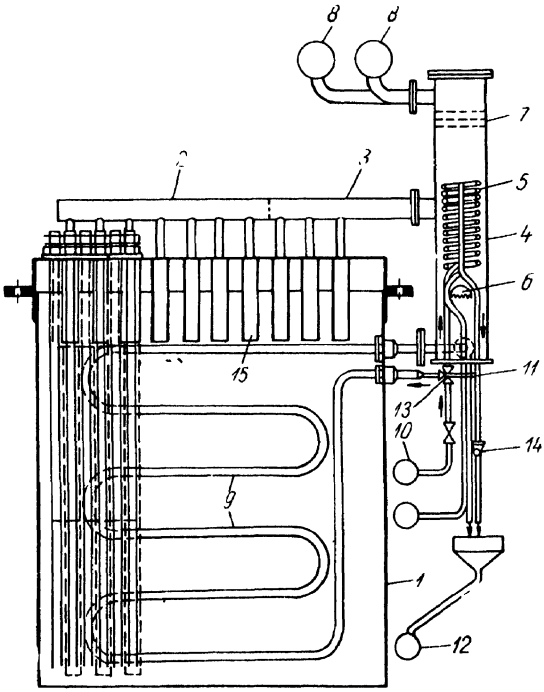


Fig. 72. Electrolyzer V – 3.

1 — Electrolyzer tank, *2* — Oxygen collecting pipes, *3* — Hydrogen collecting pipe, *4* — Cooling columns, *5* — Cooling coils, *6* — Distributor, *7* — Grid for foam disintegration, *8* — Collecting piping, *9* — Electrolyzer cooling coil, *10* - Water piping to the absorption column coil, *11* — Water piping to the electrolyzer coil, *12* — Cooling water outlet piping, *13* — Cock, *14* — Cock, *15* — Collecting bells.

distributor *6*, bubble through the water column, cooled by coil *5*, and pass through grid *7* (to disintegrate the foam) to the collecting pipe *8*. The electrolyzer is cooled by coil *9*, to keep the temperature at 70 °C. The cooling water first flows from pipe *10* to the cooling column coils, then through pipe *11* to the electrolyzer coils, and then flows away through outlet pipe *12*. If necessary, the electrolyzer cooling can be shut off by cocks *13* and *14*.

The gas absorption columns at the same time automatically feed distilled

water to the electrolyzer, maintain a stable electrolyte level in the electrolyzer and equalize the pressure of hydrogen and oxygen in the collecting bells.

With all of the electrolyzers so far described the power consumption of one electrolytic tank does not exceed 35 to 40 kw. For large gas production it will be necessary to assemble the plant from a large number of electrolyzers. Such an arrangement will require great floor space, considerable quantities of copper for the bus-bars and current distributing conductors, long and rather complicated piping, and in addition the operation and control will be rather difficult. On the other hand, when constructing small units the choice of the direct current generating unit to supply a sufficiently large current at a comparatively low voltage will cause difficulties. These reasons have recently led to the increasing use of bipolar electrolyzers in the place of monopolar ones, though the latter are of simple design, easy to assemble and repair.

2. Electrolyzers with bipolar electrodes

a) *Tank electrolyzers*

With electrolyzers of this type the tank must be designed in such a way, so that it will not conduct the current. The electrodes must divide the entire space into a series of cells (compartments) which are carefully insulated. The feeding water inlet to the separate compartments must be as small as possible to reduce the current losses caused by short circuits across the electrolyte, to a bare minimum.

This problem of an electrically non-conducting tank was solved by the firm of *Elektrizitäts A. G., formerly Schuckert*, by assembling it from several metallic parts joined together by non-conducting materials.

The bottom and the longitudinal walls of the electrolyzer (see Fig. 73) are composed of two rows of channel irons placed at a certain distance apart. In the outer compartment the channel irons are laid with the open sides pointing to the inside of the tank, in the inner compartment the channel irons are reversed. The edges of the channel irons interlock and overlap without touching. The gaps are cemented and act as insulation. In more modern designs the channel irons are separated by rubber which is a perfect insulator, whereas the cement after being impregnated by the electrolyte conducts current to a certain extent. To the terminal channels plates S_3 and S_4 are welded which form the side walls of the tanks. Thus, a compact open tank is made with electrically non-conductive longitudinal walls and bottom. On the inside of the longitudinal walls between the adjacent iron channels there are grooves into which the bipolar electrodes and diaphragm containing frames are inserted.

The middle iron plates e_1, e_2 etc. act as bipolar electrodes, and have on both sides extended perforated sheets n. The terminal monopolar electrodes have only one sheet n each. The diaphragm frame holds the asbestos cloth. The top edges of the electrodes and diaphragm frames have angle irons a, b, which are riveted and form a flat surface beneath the electrolyte level. This surface is

covered by asbestos cloth *c*, which has holes for the outlet of the gases. Over each individual compartment between the diaphragm and the electrode a long narrow gas collecting bell *g* is placed the lower edge of which is pressed against

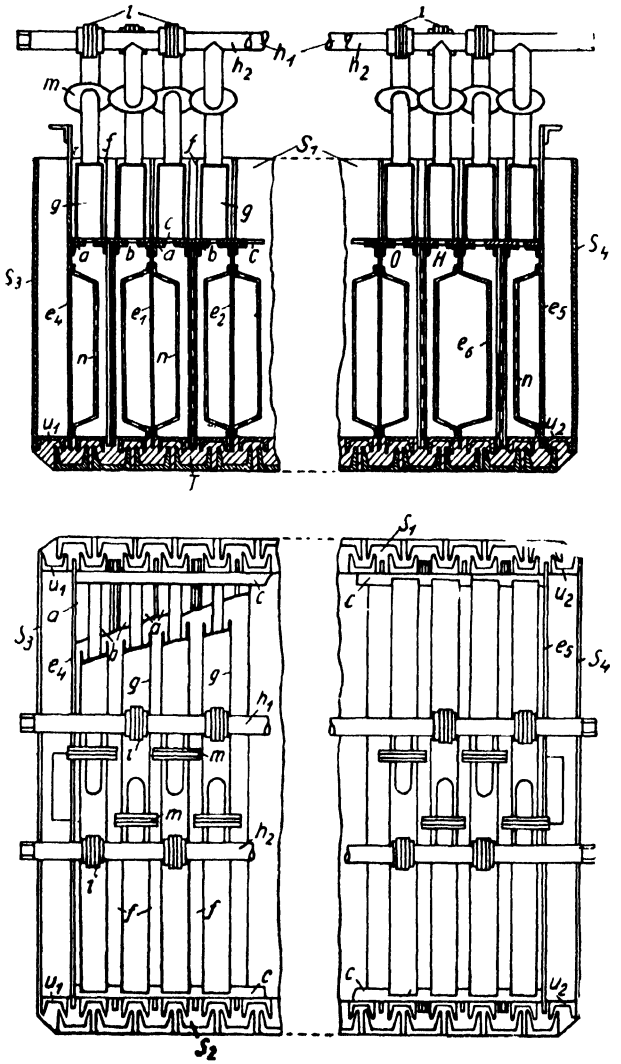


Fig. 73. Electrolyzers of the type AEG (Schuckert):

a, *b* — Angle irons, *c* — Asbestos cloth, e_1, e_2 — Bipolar electrodes, e_4, e_5 — Monopolar end electrodes, S_3, S_4 — Side walls of the tank, *T* — System of channel irons on the tank bottom, *g* — Gas pipes, h_1, h_2 — Collecting main, *n* — Extended perforated sheets, S_1, S_2 — System of channel irons at the longitudinal wall.

the asbestos cloth *c*. The gases are led to the collecting piping from the bell and flow to the gas washers and then to the gas holders.

The electrolysis temperature is 60 to 70 °C. At a current density of 5 to 6 A/sq. dm, the voltage across one compartment will be 2.1 to 2.2 V. The hydrogen obtained is 99.9% pure and the oxygen approximately 98%. The

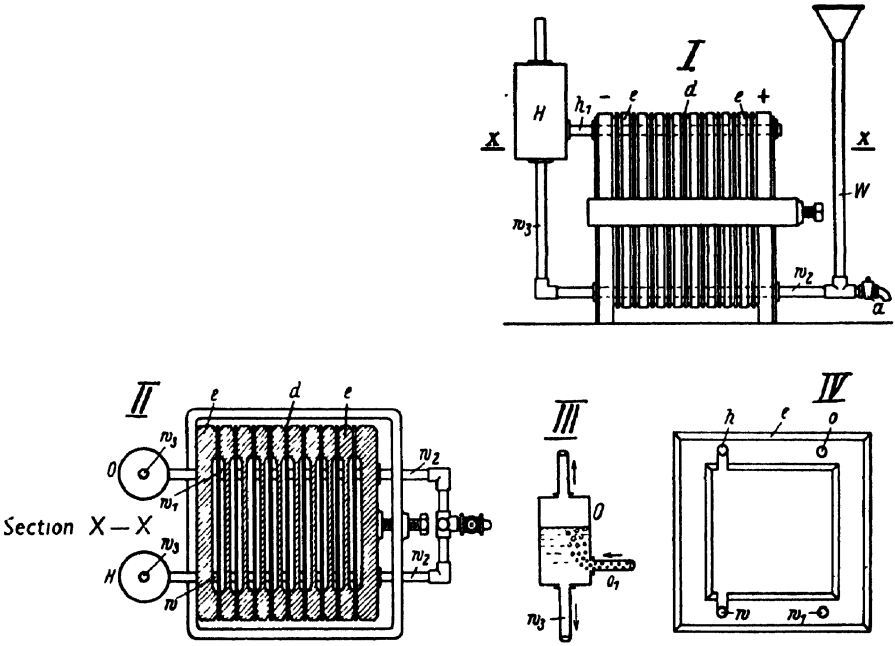


Fig. 74. Schmidt's filter-press electrolyzer with bipolar electrodes.

I — General view of the electrolyzer, *II* — Cross section *X*—*X*, *a* — Draining cock, *d* — Asbestos cloth (diaphragm), h_1 — Hydrogen outlet to separator, *H* — Hydrogen separator, *O* — Oxygen separator, w_2 — Piping for the returned electrolyte, w_3 — Distilled water inlet, *W* — Distilled water funnel, *III* — Schematic diagram of gas separator, *O* — Separated gas, o_1 — Inlet of the foaming electrolyte, w_2 — Piping for the returned electrolyte, *IV* — Middle frame of the electrolyzer, *w*, w_1 — Inlet of the electrolyte, *h* — Hydrogen outlet, *o* — Oxygen outlet.

power consumption at a current density of 5 A/sq. dm. with potassium hydroxide as electrolyte is 5.7 kw-hr. for 1 cu. m of hydrogen (at 0 °C and 760 mm Hg).

This electrolyzer usually has 15 electrodes and 14 diaphragms and the total voltage is in the range of 28 to 30 V.

b) *Filter-press electrolyzers*

The *Schmidt* type electrolyzer consists of a series of frames *e*, with a nickel plated iron plate inside which acts as electrode (see Fig. 74). Each frame has two holes *w*, w_1 at the lower corners for the inlet of the electrolyte, and two

further holes at the upper corners for hydrogen and oxygen outlet. The frames with rubber bordered asbestos cloths inserted between them provided with four corresponding holes are bolted together between the two front plates to which the current is conducted. In this way the electrolyzer forms a row of cells which are connected in series and in which every electrode acts as a bipolar conductor with the exception of the terminal ones. By clamping the frames together the holes coincide and form channels which run the entire length of the electrolyzer. One top and one bottom channel in each anode compartment are connected

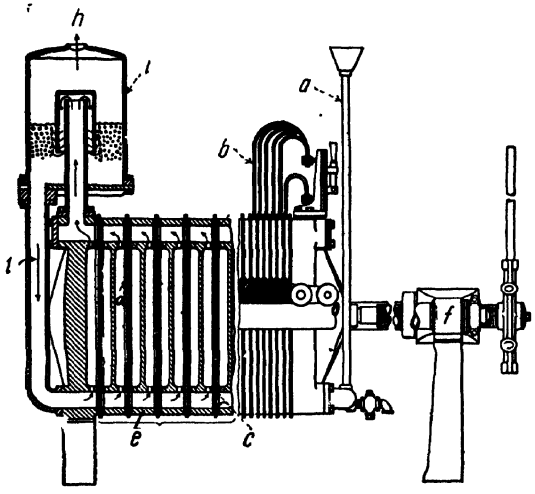


Fig. 75a. Filter-press electrolyzer.
a — Inlet of distilled water, *b* — Current conductors, *c* — Rubber insulating packing, *d* — Diaphragms, *e* — Frames containing bipolar electrodes, *f* — Frame clamping device, *h* — Gas outlet from the separator, *i* — Separator, *l* — Recirculated electrolyte.

with the corresponding holes in the frame; analogously the second two channels are connected within the cathode compartment. Both top channels are connected through pipes h_1 and o_1 with the hydrogen and the oxygen separators respectively. The entire system is filled to half of the height of the separators with electrolyte. The hydrogen and the oxygen escape from separate compartments to separators H and O carrying with them some electrolyte in the form of a fine mist; in the separators the mist is trapped and the electrolyte returns through two pipes w_3 to the bottom channels of the electrolyzer. The pure gases leave through the top of the separators. Hence the electrolyte is continuously circulating in the electrolyzer in two separated circuits. The distilled water required is fed to the bottom part of the electrolyzer by funnel X and pipings W and w_2.

This electrolyzer has usually square electrodes of approximately 900 sq. cm in

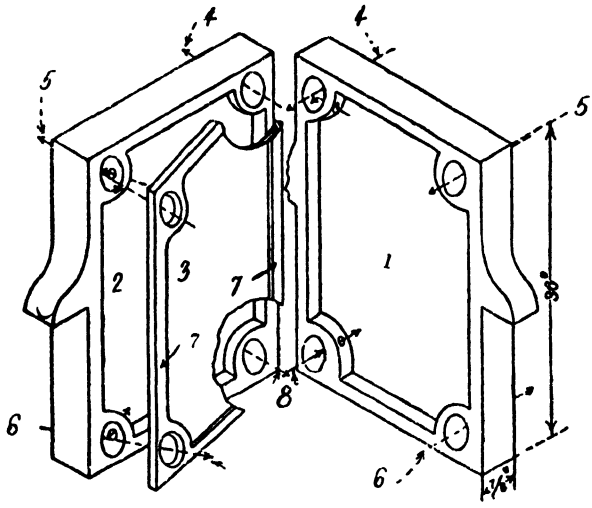


Fig. 75b. Schematic arrangement of a compartment of a bipolar filter press electrolyzer.

1 — Cathode surface on which hydrogen is deposited, *2* — Anode surface on which oxygen is deposited, *3* — Asbestos diaphragm, *4* — Connecting holes for the hydrogen (containing foam), *5* — Connecting holes for the oxygen (containing foam), *6* — Holes through which the electrolyte free of oxygen recirculates, *7* — Rubber packing, *8* — Holes through which the electrolyte free of hydrogen recirculates.

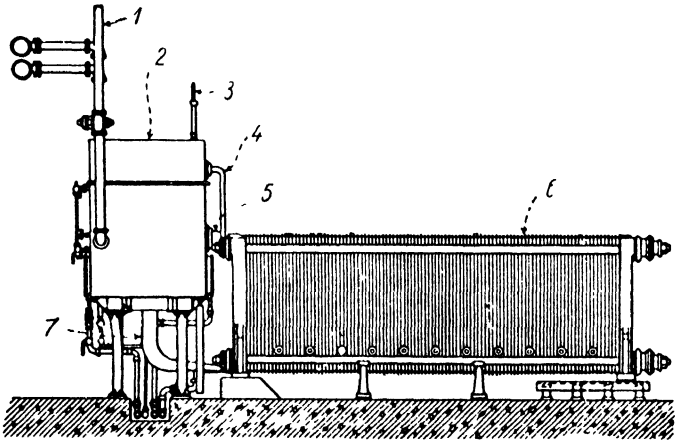


Fig. 76. Pechkranz electrolyzer.

1 — Gas outlet, *2* — Separator, *3* — Distilled water inlet, *4* — Compensating tube, *5* — Outlet of the foaming electrolyte containing gas (to the separator), *6* — Electrodes and diaphragms, *7* — Recirculated electrolyte.

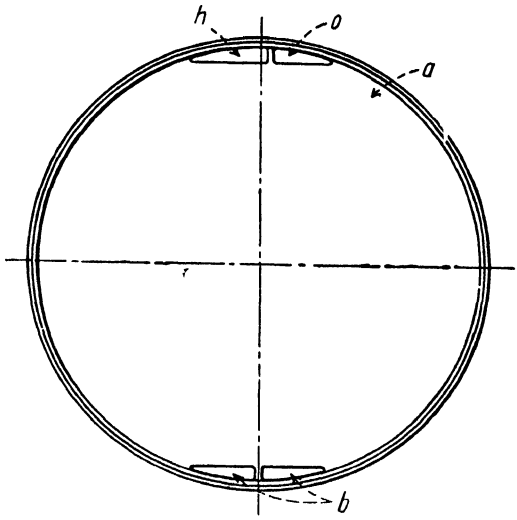


Fig. 77. Electrode of the Pechkranz electrolyzer.
a — Steel plate, *b* — Holes for inlet of recirculated electrolyte, *h* — Hydrogen outlet channel, *o* — Oxygen outlet channel.

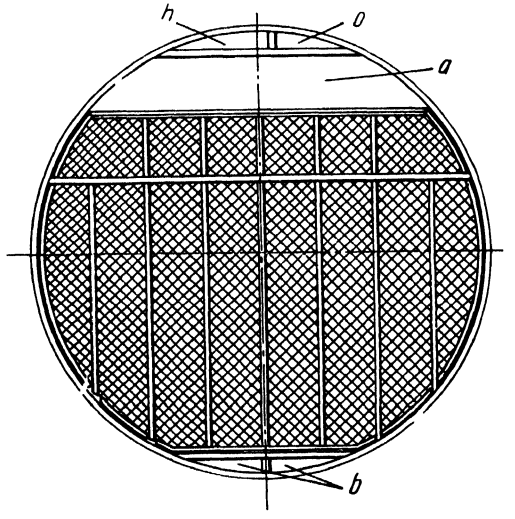


Fig. 78. Perforated nickel diaphragm of the Pechkranz electrolyzer.
a — Unperforated part of the nickel foil, *b* — Holes for inlet of recirculated electrolyte, *h* — Hydrogen outlet channel, *o* — Oxygen outlet channel.

area, roughly 2 cm thick, and has a current capacity of about 300 A. It usually consists of 61 plates forming 60 compartments. Total voltage is approximately 120 V, or in other words 2 V per one compartment.

The filter-press electrolyzer, shown in Figs. 75*a*, *b*, is of a somewhat different design.

Pechkranz devised the cylindrical electrolyzer shown in Fig. 76. The electrodes are formed by a flat circular plate which is nickel plated on the anode side. On the upper part there are two holes for the gas outlets and on the bottom two holes for the inlet of the electrolyte to anode and cathode compartments (see Fig. 77). The diaphragms (see Fig. 78), mounted in a nickel plated iron frame are made of a nickel foil 0.1 mm thick and are perforated by a great many holes. The upper part of the diaphragm above the electrolyte level is not perforated in order to prevent the gases mixing. The diaphragm frame is provided with holes for the outlet of the gases and for the inlet of the electrolyte. In between the electrodes and the diaphragms insulating asbestos spacers soaked with bitumen are inserted while the electrolyzer is being assembled. The whole system of the electrodes and the diaphragms is clamped together by long external bolts between two steel

plates one of which is stationary while the other can move on rollers.

The gas and electrolyte mixture flows through two openings in the front plate and passes to separator where the gas is separated from the electrolyte. The gases are then washed with distilled water and led to the gas holders. The hot electrolyte flows to the coolers and after cooling passes to the lower channels of the electrolyzer and then to the individual chambers. The feeding water is brought by a funnel to the upper part of the separator where it is first used to wash the gas. The separating columns connected by an overflow pipe also act as pressure controllers.

Large electrolyzers are usually composed of up to 150 compartments. An electrolyzer with 110 compartments and with the electrodes 1.8 m in diameter would be 8 m long and weigh approximately 30 000 kg. The total voltage across the terminals is 280 V at a mean voltage of 2.5 V per one compartment. These electrolyzers operate at current densities of 6.5 to 7.0 A/sq. dm and at a temperature of 65 to 80 °C. A solution of potassium hydroxide is used as electrolyte. When the electrolyzer is in good working order the voltage across one compartment is 2.35 to 2.4 V; during operation, however, the foil perforations get clogged and the voltage rises to 2.5—2.6 V. The electrolyzer yields H_2 99.2 to 99.6% pure and O_2 98.0 to 98.7% pure.

In large installations the *Bamag* type electrolyzer is very popular. A schematic arrangement of the Bamag bipolar electrodes is shown in Fig. 79. Each compartment of this filter-press electrolyzer is composed of a frame *1* with a rectangullar cross section which is welded from *T* irons. To the projecting rib of the frame diaphragm *3* is fastened which is made of asbestos cloth reinforced by interwoven fine nickel wire. The central iron plate and the two extended perforated sheets fastened to it act as electrode *4*. Between the frames and the electrodes insulating packing spacers are inserted. All metal parts of the electrolyzer are nickel plated; the surface of the cathode is activated by a special method in order to suppress hydrogen overvoltage. In the upper part of the frames are holes for the outlet of the gases which flow through pipes *7* to the collecting rings *8* and form after assembly a gas channel; the rings are mutually insulated to prevent any short-circuits which would arise if the gas channels should become connected in parallel with the individual compartment of the electrolyzer. The gases and the entrained electrolyte are separated in channels *8*.

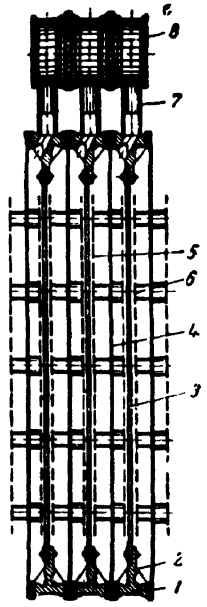


Fig. 79. Bamag type of bipolar electrolyzer with extended electrodes.
1 — Frame, *2* — Frame rib, *3* — Diaphragm, *4* — Electrode middle plate, *5* — Extended perforated sheets (the electrodes proper), *6* — Support of perforated sheets, *7* — Gas outlets, *8* — Collecting rings forming the channel.

In Fig. 80, the individual compartments *1* amounting to 100—160 are assembled as a whole and clamped tightly together by four steel bolts *3* between two massive end plates *5*. The whole electrolyzer is mounted on huge porcelain insulators *8* which support two bottom clamping bolts *3*. After assembling the electrolyzer the collecting rings *9* will form the gas flow channels and side rings *10* will form the channel for the recirculation of the electrolyte.

In the middle of the electrolyzer there is a central compartment *4* where the circulating electrolyte is cooled and filtered in filter *11*. This compartment has

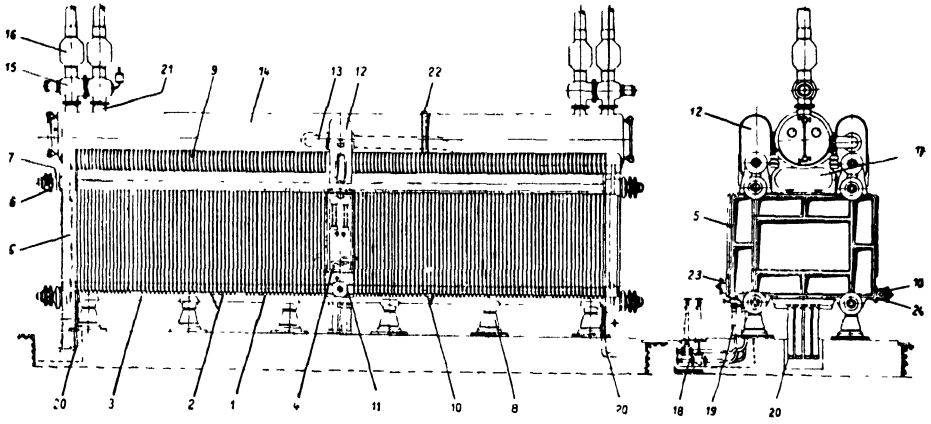


Fig. 80. Bamag type filter-press electrolyzer.

1 — Compartments, *2* — Porcelain shoe, *3* — Bolts, *4* — Central compartment, *5* — End plates made of cast steel, *6* — Spring, *7* — Porcelain plates, *8* — Porcelain insulators, *9* — Gas channel, *10* — Channel for electrolyte recirculation, *11* — Electrolyte filter, *12* — Gas collecting domes, *13* — Pipes connecting gas domes and washing drums, *14* — Gas cooling and washing drums, *15* — Gas outlet valves, *16* — Glass insulators, *17* — Electrolyte tanks, *18* — Cooling water valve, *19* — Glass piping for cooling water inlet, *20* — Current connection to end electrodes, *21* — Safety pipe, *22* — Partition in drums, *23* — Stop valve, *24* — Stop valve.

two domes *12* from which the hydrogen and oxygen is lead through pipes *13* into the large collecting, cooling and washing drums *14*. The ends of both drums have gas outlet valves *15* and safety pipes *21*; underneath are hydroxide solution tanks *17* which are connected with the central chamber *4*, where the electrolyte is cooled and separated from the gas. The cooling water enters the central compartment *4* through valve *18* and pipe *19*. The current is supplied to both end electrodes by cables *20*.

After switching on the current the hydrogen and oxygen rises into channels *9* where the gases are separated from the entrained electrolyte. The gases flow through the gas channels into the domes *12* and from there through pipes *13* into cooling drums *14*. The drums are divided by a partition *22* into two unequal sections. The larger for hydrogen and the smaller for oxygen. Here the gases are washed by distilled water to be purified of any remnants of the electrolyte

as well as cooled. The purified and cooled gases are finally drawn off through valves *15*. Both drums are connected by an overflow pipe to compensate the difference of pressure between the anode and cathode spaces of the electrolyzer.

The electrolyte separated from the gases in gas channels *9* flows to central compartment *4*, where it is cooled by means of inserted cooling coils. In the bottom part of the compartment the cooled electrolyte passes through filter *11* where the asbestos fibres from the diaphragm are removed and the electrolyte is then returned by the collecting side channel *10* to the electrolyzer compartments.

As soon as the electrolyzer starts to operate a great quantity of gases are evolved which forces the electrolyte into the hydroxide solution tank *17*; this enables to operate the electrolyte at full capacity. First the distilled water is led to the gas drums, where it washes the gases and only after this it is added to the electrolyte. The feeding water inlet and the cooling are automatically controlled so that the operator has only to watch the measuring instruments and the gas purity.

An electrolyzer with a capacity up to 500 cu m. per hour consists of 160 chambers, is 12 m long, 2.6 m wide and 5 m high. At a current load of 7500 A the electrodes operate with a current density of 25 to 30 A/sq. dm. When a 26—27% solution of KOH is used as electrolyte at a temperature of 75 to 80 °C, the voltage across one compartment will be approximately 2.2 V and across the entire electrolyzer 350 V; the power input will then be 2600 kw; the power consumption necessary to produce 1 cu. m of hydrogen will range from 5.3 to 5.4 kw-hr. The hydrogen produced is 99.9% pure and the oxygen 99.5—99.8% pure.

D. PRESSURE ELECTROLYSIS OF WATER

Should electrolysis of water be carried out in a sealed tank, completely filled with the electrolyte, gases would accumulate in the electrolyzer under a gradually increasing pressure until the maximum value of 1868 atm. at 0 °C would be reached*). At this moment the volume of the compressed gases would equal the volume occupied by the water before electrolysis. The possibility of obtaining compressed gases in the electrolyzer proper has attracted the attention of engineers for a long time because the solution of this problem would render the compression of gases prior to bottling in steel containers quite unnecessary. The solution of this question was greatly incited when it was observed that the voltage across the electrolyzer at constant current is not higher at high gas pressures, but even somewhat lower than at normal pressures.

The relation between voltage necessary for water decomposition and the pressure of gases produced is shown diagramatically in Fig. 81. From this it

*) The value 1868 atm. is only approximate as it was calculated from the equation of state $PV = nRT$ which at higher pressures does not apply any longer.

can be seen that up to a gas pressure of 30 to 40 atm. the voltage decreases more rapidly than at higher pressures. Thus e. g. in an electrolyzer working at current load 1500 A the voltage will drop by 0.33 V during a pressure increase from 1 to 40 atm. while at further pressure increase from 40 to 200 atm. the voltage drop will be 0.07 V only.

Current efficiency at higher pressure diminishes somewhat; this is possibly caused by the solubility of gases evolved in the electrolyte which is greater than at atmospheric pressure so that recombination of both gases to water is more probable.

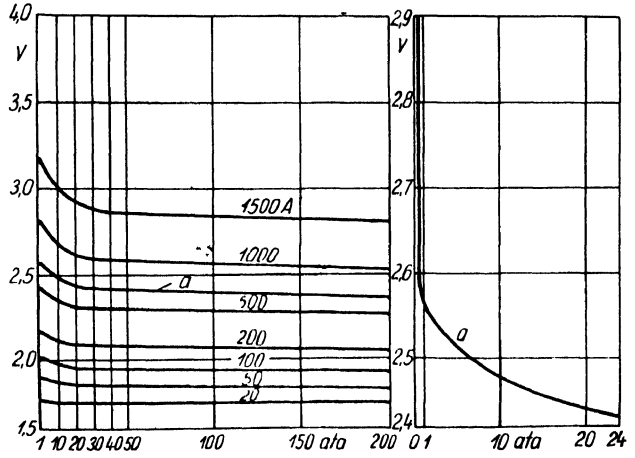


Fig. 81. Dependence of electrolyzer terminal voltage on gas pressure at varying current loads.

The drop of water decomposition voltage and the decrease of current efficiency are mutually compensated so that a certain amount of the gas produced will require the same energy consumption, or only somewhat lower, at increased pressure, as at atmospheric pressure.

The decrease of the decomposition voltage is at first sight difficult to comprehend and it cannot be explained by Nernst's equation, according to which the equilibrium deposition potentials of hydrogen and oxygen increase with increased pressure. The equation (X—8) expresses the relation between the reversible water decomposition potential and the gas pressure at 25 °C:

$$(E_R)_t = 1.229 + \frac{0.05915}{2} \log p_{H_2} p_{O_2}^{\frac{1}{2}}.$$

When both gases are evolved under the same pressure $p_{H_2} = p_{O_2} = p$ atm. the above equation will be simplified to the form:

$$(E_R)_t = 1.229 + 0.0435 \log p. \qquad \text{(X-13)}$$

This equation shows that, theoretically the water decomposition potential will rise by 0.0435 V at a pressure increase from 1 to 10 atm., or from 10 to 100 atm.

As, consequently, at pressure electrolysis the equilibrium voltage does not diminishes, the lowering of the decomposition voltage must be a result of the changed conditions under which the simultaneous irreversible processes take place. First of all it is the lower resistance of the electrolyte caused by the fact that gas bubbles are reduced in volume at a high pressure as compared with atmospheric pressure. A higher pressure has also a favourable influence as it reduces the polarization overvoltage which accompanies the deposition of gases

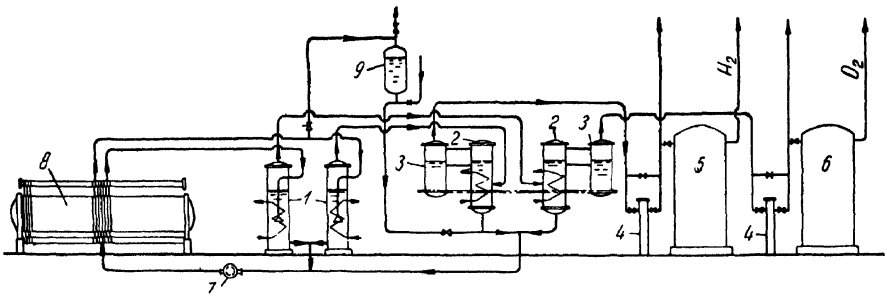


Fig. 82. Electrolyzer for producing hydrogen and oxygen at a pressure of 8 to 10 atm.

1 — Separating columns, *2* — Scrubbers, *3* — Controllers, *4* — Drying towers, *5*, *6* — Gasholders, *7* — Filter, *8* — Electrolyzer, *9* — Distilled water tank.

at both electrodes and probably it also increases the electric conductivity of the electrolyte.

From the practical point of view these electrolyzers can be divided into apparatuses producing hydrogen and oxygen at a medium pressure (8 to 10 atm.), and apparatuses operating at a high pressure of 150 to 200 atm.

The electrolyzer designed by Soviet technicians is an example of the first kind. This electrolyzer (Fig. 82) consists of one hundred cells with bipolar electrodes clamped together by four bolts between the iron end plates. This apparatus is fed with a current of 200 A from the mercury rectifier at a voltage of 240 V and produces 8.5 cu. m of hydrogen per hour. There are two gas collecting channels above the electrolyzer and below a channel for inlet and distribution of the electrolyte to the individual cells. The gases together with the electrolyte enter separating columns *1*, where at the same time their pressure is accurately equalized. After the electrolyte has been separated the gases are led into washing towers *2*, where they are washed and cooled. From the washing towers the gases pass through float type controllers *3*, where their pressure is again equalized to the towers *4* where they are dried by means of calcium chloride; finally they are led to gasholders *5* and *6*. The electrolyte after being

cooled in the separating column is recirculated in the electrolyzer through filter 7. The distilled water from tank 9 first flows to the washing towers 2 and then together with the electrolyte to the electrolyzer.

After passing from the electrolyzer the compressed gases are used directly for autogenous cutting and gas welding of metals. In the U.S.S.R. apart from stationary installations a mobile unit is used which is mounted on a truck. The electrolyzer is fed with current from a generator which is driven by the motor of the motor-car.

The electrolyzers operating at high pressure (150—200 atm.) are very difficult to design and construct. Primarily it is necessary to ensure the uniform removal of both gases and maintaining the constant pressure of the hydrogen and oxygen. At 200 atm. a pressure difference of only 5% would mean an absolute pressure difference of 10 atm. on both sides of the diaphragm; under such uneven stress, the brittle diaphragm would break and the gases would be mixed. Until today the problem of pressure electrolysis for large units has not been satisfactorily solved from the technical point of view; in industry only small apparatuses are to be found, and those in rather rare instances.

The firm „*Druckzersetzer*" have designed an electrolyzer yielding 21 cu. m hydrogen and 10.5 cu. m oxygen per hour at a pressure of 150 atm. In this instance there is a danger of explosion so that the electrolyzer is placed in a pit protected by concrete walls. Over the pit there is an operating platform with electric instruments and pressure controllers. The gases are filled into steel cylinders in separated shelters.

The electrolyzer consists of four high-pressure steel cylinders. Each cylinder has 80 cells connected in series, fed by a current of 150 A, at a total voltage of 160 V. The individual cylinders are connected in parallel, so that through the whole electrolyzer a current of 600 A and 160 V flows.

Each cell consists of several frames made of alkali resistant plastic between which are inserted alternately nickel gauze anodes, metal reinforced asbestos diaphragms and nickel gauze cathodes. In one cell there are three anodes and two cathodes; each electrode has its own current supply. The individual parts are assembled and tightly clamped together to form one unit, in which a series of small compartments is formed between the diaphragms and the electrodes. The holes in the frames (two at top and two at the bottom) form longitudinal channels after the frames have been put together; through the bottom channels the electrolyte is led to the anode and cathode and the hydrogen and oxygen is drawn off through the top channels. The five-electrode unit is roughly of octagonal shape and approximately 18 cm in diameter.

Eighty such units are clamped together between two end plates, and form a group which is placed in the steel cylinder and connected to the electrolyte inlet pipes, electric leads and gas collecting pipes. The channels for the electrolyte inlet and gas outlet run through the whole length of the cell group so that the separation of the liquid from the gas stream and the recirculation is common for the whole electrolyzer. To the outside steel cylinder a special oil is pressed

which fills all the space round the electrolyzer and so guarantees good insulation. Outside the cylinder are separators and gas scrubbers, compensating vessels for the electrolyte and the oil, and a regulating device for maintaining a constant pressure in the electrolyzer.

To facilitate the escaping of gases from the compartments the steel cylinders are placed at an angle of 45°. After the electrolyte is separated the gases flow through scrubbers and are then purified on pumice coated with fine dispersed palladium. Small amounts of hydrogen and oxygen respectively which are present in both gases as contaminations are removed by a catalytic reaction in the course of which they are burned to water.

There is a very ingenious device for keeping a constant pressure in the anode and cathode compartments. It is formed by two U-shaped tubes which are partly filled with mercury and are attached to a pendulum which is connected to an electric motor. A narrow pipe feeds compressed hydrogen to one arm of the U-shaped tube and another pipe feeds compressed oxygen to the other U-shaped tube. Equilibrium is maintained by compensating the hydrogen and oxygen pressure by nitrogen fed under the same and constant pressure to the other arms of both U-shaped tubes. Any change of pressure in one of the U-shaped tubes will cause a deflection from the equilibrium position; this will switch on the motor which operates the valves in the gas outlet pipes in such a way that the initial state of equilibrium will be restored again. The electrolyzer can, therefore, operate under full pressure without any regard to the operating pressure of the filling station. To maintain a continuous delivery of gases, twice the number of cylinders are filled with hydrogen than with oxygen. Great attention must be paid to the automatic control of the constant level of the electrolyte in the anode and cathode compartments. The gas purity is controlled by automatic recording instruments.

E. USES OF HYDROGEN AND OXYGEN

Hydrogen is used commercially in the manufacture of ammonia and hydrogen chloride, for the production of liquid fuels from coal, for hydrogenation processes (especially for hydrogenation of fats), for autogenous cutting and welding of metals by oxy-hydrogen flame, for lead soldering, for the production of artificial precious stones, etc.

Hydrogen for commercial use is compressed to 150 atm and distributed in steel cylinders marked red, equipped with left threaded armatures. Electrolytic hydrogen contains 1 to 2% oxygen, which can easily be removed by leading it through platinized asbestos at a temperature of 400 to 500 °C.

In industry oxygen is used for the manufacture of concentrated nitric acid and for the production of pure carbon monoxide from which formic acid is manufactured, for autogenous welding and cutting of metals, in oxygen respirators, for the processing of quartz and platinum, for the production of artificial precious stones and in laboratories. Recently oxygen has been increasingly used

in the manufacture of gaseous fuels and in metallurgy for intensifying some metallurgical processes (e. g. for production of pig iron and maleable iron).

Oxygen compressed to 150 atm. is sold in steel cylinders marked blue. When oxygen is required in a large amount it is supplied in liquid form. This makes it much easier to transport and saves transportation cost, which is considerable in the case of steel cylinders filled with compressed gas. Liquid oxygen is transported in special steel tanks mounted on railway waggons. The tanks are spherical in shape, to keep their surface area as small as possible and are covered on the outside by insulating material.

XI. CHLORINE AND ALKALI HYDROXIDES

Chlorine at normal temperature and atmospheric pressure is a yellow-greenish gas heavier than air (1 lit. of gas weighs 3.2204 g at 0 °C and 760 mm Hg). When cooled it condenses to form a liquid boiling at —34 °C (at 760 mm Hg); at —102 °C it solidifies into a yellow cristalline substance. The critical temperature of chlorine is 144 °C and the critical pressure 76.1 atm. Chlorine dissolves comparatively well in water, but its solubility is considerably reduced by the presence of sodium chloride. Chlorine dissolves better in organic solvents than in water, e. g. in dichlorethane, carbon tetrachloride etc.

Chlorine is chemically very active. At appropriate temperatures it combines directly with many metals and metalloids. In an aqueous solution chlorine hydrolyses, especially when exposed to daylight, into hydrochloric and hypochlorous acids. The last mentioned acid is further decomposed into hydrochloric acid and oxygen which is a strong oxidizing agent. Chlorine water and moist gaseous chlorine are, therefore, powerful bleaching agents. The considerable corrosive effect of moist chlorine on metals can also be explained by its hydrolysis. On the other hand, dry chlorine at a normal temperature has practically no effect on iron, copper, lead etc. Mixtures of chlorine and hydrogen explode when exposed to sunlight in presence of catalysts, or at higher temperatures. The mixture becomes explosive when it contains 14.5% to 91.9% hydrogen.

Two compounds of oxygen and chlorine are known chlorine monoxide and dioxide. When chlorine dioxide reacts with solutions of bases, chlorates are formed as well as salts of chlorous acid which are popular bleaching agents.

When chlorine is brought into contact with solutions of alkali hydroxides hypochlorates or chlorates are formed in addition to chlorides, according to the reaction conditions. Chlorates may be thermally decomposed to form salts of perchloric acid.

Chlorine in the technical sphere is very widely applied. The most important of these applications are:

1. oxidation,
2. chlorination of organic compounds,
3. chlorination of metal oxides and non metallic compounds,
4. disinfection and sterilization.

In the chemical industry chlorine is used for the production of various chemical compounds, such as hydrochloric acid, hypochlorites, chlorates, bleaching powder, aluminium chloride, corrosive sublimate, cupric chloride, carbon tetrachloride, tin recovery from used cans, sulphuryl chloride, for extraction of bromine from Stassfurt waste liquors, etc. In the organic chemical industry it is used for the chlorination of aliphatic and cyclic organic compounds, for the preparation of medicaments, the manufacture of plastics, insecticides, fungicides and herbicides. Monochloracetic acid, ethylene chlorhydrine, chloral, chlor-

benzene, vinyl chloride, vinylidene chloride, chlorinated rubber, dichlorostyrene, chlorinated polyethylenes, dichlordiphenyl trichlorethane (DDT), hexachlorcyclohexane, dichlorophenoxyacetic acid, pentachlorophenol, dichlorbenzen etc, are among these substances.

In the fat and oil industry chlorinated compounds are used as organic solvents for the extraction of fats, in the textile and paper industries chlorine is used for bleaching textiles and cellulose, in metallurgy for the chlorination of ores and in pyrotechnics chlorates are used as oxidizing agents. Chlorine is of the utmost importance for the disinfection of water and for purifying and sterilizing drinking and waste water.

A. CHEMICAL METHODS IN THE MANUFACTURE OF CHLORINE

Chlorine was at first produced commercially by the reaction of sulphuric acid, sodium chloride and black oxide of manganese. Later on when Leblanc's method for the production of soda ash was developed, in the first stage of which hydrogen chloride is a by-product, hydrochloric acid was used instead of sodium chloride and sulphuric acid. This process was carried out in stoneware or porcelain vats which were steam heated from the outside. Reaction between manganese dioxide and hydrochloric acid proceeds in two stages:

$$MnO_2 + 4HCl = MnCl_4 + 2H_2O, \qquad (XI\text{-}1)$$

$$MnCl_4 = MnCl_2 + Cl_2 \qquad (XI\text{-}2)$$

Great progress was made when *Weldon* invented a method for recovering manganese dioxide from waste liquors. By this method calcium hydroxide was added to the liquors which remained after oxidation of hydrochloric acid·

$$2MnCl_2 + 2Ca(OH)_2 = 2CaCl_2 + 2Mn(OH)_2, \qquad (XI\text{-}3)$$

whilst through the resultant pulp air was bubbled:

$$2Mn(OH)_2 + Ca(OH)_2 + O_2 = CaO \cdot 2MnO_2 + 3H_2O \qquad (XI\text{-}4)$$

The precipitated slurry, containing $CaO \cdot 2MnO_2$, called the Weldon mud was then used instead of black oxide of manganese for the oxidation of hydrochloric acid. This reaction which was carried out in sandstone containers with steam fed into the reaction mixture proceeded according to the equation:

$$CaO \cdot 2MnO_2 + 10HCl = 2Cl_2 + 2MnCl_2 + CaCl_2 + 5H_2O. \qquad (XI\text{-}5)$$

The utilization of hydrochloric acid amounted to 40% a maximum, the rest being lost as calcium chloride.

Another old method is the *Deacon-Hurter* process which is based on the oxidation of gaseous hydrogen chloride by atmospheric oxygen in contact with

pieces of brocken bricks soaked with cupric chloride which acts as a catalyst:

$$4HCl + O_2 = 2H_2O + 2Cl_2. \qquad \text{(XI-6)}$$

As this is an exothermic reaction the yields are the greater the lower the operational temperature. If the rate of reaction is to be kept sufficient the temperature must not drop below 450 °C. During this process a mixture of concentrated hydrochlorid and sulphuric (62 °Bé) acid was heated and the evolved hydrogen chloride was displaced by air so as to obtain a gaseous mixture containing 40% HCl and 60% of air. After cooling and drying in a scrubber with concentrated sulphuric acid this mixture was preheated and passed through a contact chamber where pieces of broken bricks impregnated with cupric chloride solution were strewn on the perforated bottom. The gas was first led to an absorption equipment in order to remove the remaining hydrogen chloride in the form of hydrochloric acid and, finally, washed by concentrated sulphuric acid to remove all moisture.

The yield of chlorine was higher than with Weldon's process (i. e. about 69 p. c.), but there was a disadvantage because the chlorine produced was very diluted being mixed with nitrogen. For this reason it was only used for the production of bleaching powder, but not for liquefaction.

The *Atmospheric Nitrogen Corporation* in the USA have developed a process by which the chlorine in addition to sodium nitrate is produced from common salt and oxides of nitrogen obtained from ammonia oxidation. This is done in a reaction tower where the following reactions take place:

$$6\ NO_2 + 2H_2O = 4\ HNO_3 + 2\ NO$$
$$3\ NaCl + 3\ HNO_3 = 3\ NaNO_3 + 3\ HCl$$
$$3\ HCl + HNO_3 = Cl_2 + NOCl + 2\ H_2O$$
$$2\ NO + Cl_2 = 2\ NOCl.$$

The whole process in the reaction tower can be expressed by a summary equation

$$NaCl + 2\ NO_2 = NaNO_3 + NOCl \qquad \text{(XI-7)}$$

from which it is evident that nitrosyl chloride is the main component of the gas mixture after reaction. This is an exothermic reaction so that a higher temperature would lower the yields; therefore, the temperature in the reaction tower should not exceed 60 °C.

The gas mixture escaping from the tower first of all enters a cooler to condense the water vapour. The dry mixture which contains less than 0.1% of water vapour is then mixed with oxygen and led to the oxidation reactor, where in the presence of a catalyst the following reaction is allowed to proceed at a temperature of 300 °C:

$$2\ NOCl + O_2 = Cl_2 + 2\ NO_2. \qquad \text{(XI-8)}$$

The products of oxidation are liquified at —50 °C and the remaining gaseous oxygen is returned to the oxidation reactor. The liquid which contains nitrogen dioxide, chlorine and a small amount of the unreacted nitrosyl chloride will be separated in a fractionating column into gaseous chlorine, the final product which is drawn off from the top of the column, as well as a liquid solution of nitrogen oxides and nitrosyl chloride. Finally, this solution is vaporized and, after further oxides of nitrogen have been added, returned to the reaction tower. At first great difficulties were encountered during the course of operation owing to the problems of corrosion. These were finally overcome by using absolutely dry gases and ceramic construction material. A factory in Virginia uses this method of production.

B. ELECTROCHEMICAL METHODS IN THE MANUFACTURE OF CHLORINE

The most important and now almost the sole industrial method of manufacturing chlorine is the electrolysis of alkali chloride solutions during which hydrogen and alkali hydroxide are also produced. Often hydroxide production is more important so that chlorine is then a by-product. It is sometimes difficult to find a suitable market for chlorine. In those countries where the manufacture of chlorinated organic derivatives (primarily plastics) is a developed industry the situation is just the reverse and here the demand for chlorine is much greater than for hydroxides.

1. Raw materials for electrolytic manufacture of chlorine and hydroxides

The basic raw materials for the manufacture of chlorine are solutions of sodium or potassium chloride, which are usually prepared at the place of manufacture by dissolving solid salts; in some factories the base is the natural sodium chloride brine.

The initial raw material should contain the minimum impurities and admixtures of sulphates, calcium and magnesium salts. A sodium chloride solution is applied in a saturated state; potassium chloride solutions are generally unsaturated to prevent the danger of the pipes becomming clogged at an unexpected cooling of the solution as the solubility of this salt depends to a considerable degree upon the temperature.

a) *Sodium chloride*

Rock salt, salt from natural brine and salt from the sea or lakes are the sources of common salt.

The majority of salt is mined from rock salt deposits which have been created by the evaporation of water from ancient seas. There are no substantial rock

salt mines in Czechoslovakia so that salt must be imported from Germany (from the large salt producing area round Stassfurt) and from the USSR (Carpathian Ukraine). Other important salt beds in Europe are the well known mines at Wieliczka in Carpathian Mountains in Poland, the mines in the provinces Marmaros and Transylvania in Rumania, Aussee, Ebensee, Hall, Ischl, Hallein and Hallstatt mines in Austria, mines in Lorraine in France, in the USSR (Brjancevskoje, Slavjanskoje, Ileckoje and Solikamskoje), in Spain (near Cordova in Catalonia), and in England (in the counties of Cheshire and Shropshire). As long as the salt mined is sufficiently pure it is immediately disintegrated to the size of grain required.

The second source of salt is from natural brines which are the result of rock salt being dissolved in ground water; such brine is either from springs (wells) or is brought to the surface of the earth by pumping. Brine can be also artificially prepared when from impure deposits the salt is leached with water. Brine is treated at salt works and cristalline salt is produced or it is used as a solution for further chemical manufacture in factories which are built in the vicinity of the brine source. If the solution is not sufficiently concentrated it is saturated by addition of solid salt.

In Czechoslovakia there is a mine at Solnohrad near Prešov which is flooded by ground water from which the brine is pumped to the salt works for the production of the cristalline salt.

The brine is evaporated either in open pans or in vacuum evaporators. When evaporation takes places in a vacuum evaporator the solution must be first freed of calcium and magnesium salts. Otherwise deposits will be formed on the boiler tubes and these would decrease the rate of heat transfer.

Sea water is an inexhaustible source of salt; one litre contains on the average 35 g of various salts of which approximately 27 g is sodium chloride. Sea water salt is obtained primarily in countries with a hot, dry climate and is a result of solar evaporation in the so called salt fields, i. e. on the coast of France, Italy, Dalmatia, Spain, Portugal, USA and Japan. A less common method of sea water processing is artificial evaporation as in Normandy or winterization as in the USA.

The water from salt lakes such as lake Baikal, lake Buskunchak, lake Elton, lake Bogdos and other lakes in the USSR, as well as desert lakes in Egypt, Libya, Algeria etc. deposit salt on the lake shore during intense heat and then it is simply showelled away.

b) *Potassium chloride*

Carnallite $KCl \cdot MgCl_2 \cdot 6H_2O$ and sylvinite which is a mixture of sodium and potassium chlorides are of the greatest technical importance as raw materials necessary to produce potassium chloride. Sylvine (KCl) is a mineral rarely found in the nature. The above mentioned minerals are not to be found in the earth in a pure form. Carnallite is usually combined with common salt, kieserite ($MgSO_4 \cdot H_2O$) and anhydrite ($CaSO_4$); sylvinite is usually contaminated by

kainite ($KCl \cdot MgSO_4 \cdot 3H_2O$), schönite ($K_2SO_4 \cdot MgSO \cdot 6H_2O$) and hard salt (a mixture of sylvine, rock salt and kieserite).

These raw materials are mined like rock salt. The potassium chloride is separated by leaching and fractional crystallization based upon the different solubility of individual components of the starting raw material.

Carnallite is generally treated so that it is dissolved in hot water or spent liquor; from this solution the undissolved salts are removed by sedimentation (mainly kieserite and common salt). The clear liquid is then cooled and the majority of the potassium chloride crystallizes out (some 80 per cent). A part of the spent liquor together with the wash water is then used to extract fresh row material. The remaining mother liquor is concentrated by evaporation and after cooling potassium chloride is separated in the form of artificial carnallite which is returned to the process. The waste liquor is either discarded or it is treated to yield magnesium salts. Sometimes bromine is extracted from waste liquor by treating it with chlorine. From the crude potassium chloride obtained the remainig sodium chloride is removed by washing with cold water.

When treating sylvinite the leaching operation is carried out at around 110 °C with hot mother liquor from the preceding operation. This mother liquor is saturated with sodium chloride, so that only potassium chloride will be dissolved from the raw material. The liquor obtained after lixiviation is separated from the insoluble residue (from the raw material) and is cooled to 20 °C in a vacuum crystallizer in order to precipitate the potassium chloride which is the least soluble salt. The crystals are then filtered off on a rotary vacuum filter and washed and dried. The mother liquor which now has a smaller content of potassium chloride but is still saturated with sodium chloride is warmed once more and used for next leaching of fresh sylvinite. The process has a cyclic character and is based on the comparatively great difference between the solubility of potassium chloride at 110 °C and at 20 °C and the negligible change in solubility of sodium chloride within this range of temperature.

Recent reports give information about a flotation process by which potassium chloride can be obtained from sylvinite. Ground sylvinite is floated in a saturated solution of potassium and sodium chloride while a suitable proportion of the solid phase and liquid phase is maintained. Solid potassium chloride containing 96 to 98 per cent KCl is carried away in the froth while common salt is discharged from the bottom. It has proved advantageous to carry out this process immediately after mining underground and to use the remnants (some 60 to 80 per cent of raw materials used) to refill the cavities caused by mining.

Czechoslovakia has no raw material of this kind so potassium chloride is imported mainly from Stassfurt (where it is prepared from carnallite) and from Alsace (where it is obtained from sylvinite) and Palestine (the Dead-Sea). In the USSR the largest deposits of sylvinite and carnallite are found in the territory between the river Kama and the Ural mountains (Solikamsk). Other potassium salt deposits are at Stebnik near Drogobycz and at Kaluga in West Ukraine. Spain has deposits of sylvinite and carnallite in Catalonia. Deposits

in the USA are in California, Western Texas, New Mexico and Utah and contain mainly sylvinite, carnallite and polyhalite. On the African continent there are important deposits at Dankalia in Ethiopia with very pure sylvine.

2. Technological processes in the manufacture of chlorine and caustics

The electrolytical methods of manufacturing chlorine and caustic are divided into two groups:

a) Methods using electrolytic cells with a solid metallic cathode;

b) Methods using electrolytic cells with a mercury cathode

These processes differ by the reaction which occur at the cathodes. At a solid cathode which is generally made of iron, hydrogen ions are discharged and simultaneously alkali hydroxide is formed in the electrolyte. At the mercury cathode metallic sodium or potassium is deposited which forms amalgam. This intermediary product is subsequently decomposed by water in a separate compartment whereby hydroxide and hydrogen are obtained while the liberated (denuded) mercury is returned into the electrolytic cell.

a) *Production of chlorine and alkali hydroxide in electrolytic cells with iron cathodes*

α) Theoretical principles

Aqueous solutions of alkali chlorides contain Na^+ (or K^+), Cl^-, H^+ and OH^- ions. On the iron cathode (or on a cathode of another solid metal) hydrogen ions can be discharged even from a strong alkaline solution and gaseous hydrogen is formed; ions of alkali metals, however, are not discharged, as the electrical work required for hydrogen deposition is much lesser. After the liberation of hydrogen the solution in the proximity of the cathode becomes alkaline, due to an excess of hydroxyl ions which combine with sodium cations to give sodium hydroxide.

Chloride ions will be discharged at a platinum, graphite or magnetite anode from saturated neutral solutions of sodium or potassium chloride rather than hydroxyl ions although at equilibrium conditions it should be the very opposite, as the reversible deposition potential (reduction potential) of oxygen in neutral solution is much lower*) ($\pi_{OH^-\,|\,O_2,\,Pt} = 0.815$ V at 25 °C) than the standard

*) The equilibrium reduction potential of an oxygen electrode is as follows:

$$\pi_{OH^-\,|\,O_2,Pt} = \pi^\circ_{OH^-\,|\,O_2,Pt} + \frac{RT}{2F} \ln \frac{p_{O_2}^{\frac{1}{2}}}{a_{OH^-}}$$

At a temperature of $T = 298{,}1$ °K we have $\pi^\circ_{OH^-\,|\,O_2,Pt} = 0{,}401$ V. At an oxygen pressure $p_{O_2} = 1$ atm. and activity of hydroxyl ions $a_{OH^-} = 10^{-7}$ (neutral reaction) we obtain

$$\pi_{OH^-\,|\,O_2,Pt} = 0{,}401 - 0{,}05915 \log 10^{-7} = 0{,}815 \text{ V}.$$

reversible potential of chlorine ($\pi_{Cl^-|Cl_2,Pt} = 1.358$ V at $p_{Cl_2} = 1$ atm. and $a_{Cl^-} = 1$). While chlorine is evolved at anodes made of the materials mentioned at a comparatively low overvoltage, hydroxyl ions are discharged at a much higher overvoltage so that the actual deposition potential of oxygen is higher than that of chlorine. This is the reason why chlorine and not oxygen is liberated at the anode in concentrated chloride solutions.

The electrochemical processes which occur during electrolysis of alkali chloride solutions can be summarized as follows:

$$2H_2O + 2e = H_2 + 2\,OH^- \text{ (cathode)} \qquad \text{(XI-9)}$$

$$2\,Cl^- = Cl_2 + 2e \text{ (anode)} \qquad \text{(XI-10)}$$

$$2\,Cl^- + 2H_2O = 2OH^- + Cl_2 + H_2 \qquad \text{(XI-11)}$$

Alkali hydroxide and hydrogen are formed at the cathode and gaseous chlorine at the anode.

During the first stages of electrolysis when the alkali hydroxide concentration is still low, only chloride and sodium ions conduct the current. If the unit quantity of electricity (1 F) passes through the solution 1 gram-equivalent of chlorine at the anode and 1 gram-equivalent of hydrogen at the cathode will be evolved. If the transference number of sodium ions is approximately $t_+ = 0.4$ and that of chloride ions $t_- = 0.6$ then the passage of the afore mentioned quantity of electricity through the electrolyte causes also a migration of 0.6 gram-equivalent of Cl^- ions from the cathodic to the anodic compartment and a migration of 0.4 gram-equivalent of Na^+ ions from anolyte to catholyte. This 0.4 gram-equivalent of Na^+ gives together with 0.6 gram-equivalent of Na^+ (which remains in the catholyte after "emigration" of 0.6 gram-equivalent of Cl^-) 1 gram-equivalent of Na^+ which then gives with 1 gram-equivalent of OH^- (which remain in the catholyte after liberation of 1 gram-equivalent of H^+) a total of 1 gram-equivalent of NaOH. This process is illustrated in the following table:

	Catholyte				Anolyte	
On beginning of the process . . .	1 Na^+	1 Cl^-	1 H^+	1 OH^-	1 Na^+	1 Cl^-
Migration . . .	+ 0.4 Na^+	− 0.6 Cl^-	0	0	− 0.4 Na^+	+ 0.6 Cl^-
Discharge . . .	0	0	− 1 H^+	0	0	− 1 Cl^-
After passage of 1 F of electricity	1.4 Na^+	0.4 Cl^-	0	1 OH^-	0.6 Na^+	0.6 Cl^-
	1 NaOH + 0.4 NaCl				0.6 NaCl	

From this it can be seen that during electrolysis the catholyte gains sodium salt which increases its specific gravity while the concentration of sodium salt decreases in the anolyte.

Current efficiency

Current efficiency is here not so high as during the electrolysis of water because it is lowered by certain side reactions which occur simultaneously while the main process takes place (see equation XI-9) and (XI-10). First of all, it is chlorine which is not entirely removed from the electrolytic cell. It is partially dissolved in the electrolyte and reacts according to the nature of the medium and gives either a very slightly dissociated hypochlorous acid or a considerably dissociated hypochlorite.

In a neutral (or acid) anolyte the following reaction occurs between the dissolved chlorine and water:

$$Cl_2 + H_2O = HCl\,O + H^+ + Cl^-. \qquad \text{(XI-12)}$$

While the catholyte becomes alkaline during electrolysis as a result of the discharge of hydrogen ions the solution at the anode, originally neutral, acquires an acid reaction due to the mentioned hydrolysis of dissolved chlorine.

Since the equilibrium of the reaction (XI-12) in a neutral medium is considerably shifted toward the left side of the equation and, moreover, hypochlorous acid is a very weak acid the quantity of hypochlorite ions formed by dissociation is negligible and so does not practically influence the course of the anodic processes.

Other conditions exist in the alkaline solution formed as soon as the hydroxyl ions set free at the cathode reach the anolyte due to diffusion, mechanical stirring or migration. Under such conditions hypochlorous acid and hydrogen ions are neutralized by hydroxyl ions to form well dissociated hypochlorite. This causes a disturbance of equilibrium in accordance with the equation (XI-12) and brings about further dissolution of chlorine in the electrolyte:

$$Cl_2 + 2OH^- = Cl\,O^- + Cl^- + H_2O. \qquad \text{(XI-13)}$$

As soon as the hypochlorite ions so formed arrive at the anode they are oxidized into chlorate ions, according to equation

$$6\,ClO^- + 6OH^- = 2ClO_3^- + 4\,Cl^- + 3/2\,O_2 + 3\,H_2O + 6e, \qquad \text{(XI-14)}$$

because they are more easily discharged than chloride ions even at a low concentration. Because of this easy oxidizability of hypochlorite ions there is nearly always a small quantity of chlorate in caustic produced in electrolytic cells with iron cathodes. The reaction (XI-14) is not desirable in the production of caustic, because quality and yield are lowered and also the oxygen set free destroys graphite electrodes.

In the limiting case, if all hydroxyl ions set free at the cathode would be transferred to the anode, a chemical reaction (see equation XI-13) would result between them and the whole amount of evolved chlorine with the subsequent electrochemical oxidation of hypochlorite ions to chlorate ions according to

equation (XI-14). Under these conditions no gaseous chlorine would be liberated at the anode because it would be consumed to form hypochlorite and chlorate.

This must not be, of course, allowed when producing alkali hydroxides (caustics). All possible measures must be taken to prevent hydroxyl ions penetrating to the anode in order to suppress the undesirable reaction (XI-13) and (XI-14). The following precautions may be applied:

To prevent the mechanical mixing of catholyte and anolyte or their mutual diffusion, both liquids are kept separated by means of a diaphragm or they are allowed to stratify according to their different specific gravities.

Another way of excluding the undesirable reactions (XI-13) and (XI-14) consists in maintaining a high chloride concentration in the electrolyte. The solubility of gaseous chlorine in a saturated brine is much lower than in a diluted solution, therefore, the equilibrium concentrations of hypochlorous acid [see the equation (XI-12)] and of hypochlorite ions in the proximity of the anode are also much lower.

Moreover, a higher temperature of the electrolyte exerts a favourable influence, as it lowers the solubility of the chlorine in the brine as well as the quantity of hydroxyl ions transferred from catholyte to anolyte (transfer number of hydroxyl ions in a normal NaOH solution equals 0.82 at 18 °C; with increasing temperature its value decreases nearly to 0.5).

Another source of anodic oxygen evolution is a direct discharge of hydroxyl ions according to equation

$$2\ OH^- = H_2O + \tfrac{1}{2}O_2 + 2e, \qquad \text{(XI-15)}$$

which occurs if the brine concentration is too low or if OH^- ions pass from the catholyte to the anode.

This reaction is as undesirable as reactions (XI-13) and (XI-14), but can be suppressed if the brine concentration is kept a shigh as possible. In such concentrated solutions the potential of the chlorine electrode becomes more negative, hence, more differentiated from the deposition potential of oxygen. Reaction (XI-15) can also be suppressed by using anode material with minimum chlorine overvoltage but a high oxygen overvoltage.

Oxygen liberation is thought to be initiated by the presence of a large quantity of sulphate ions in the solution. In order to prevent an unduly high concentration of sulphate ions during electrolysis a low concentration level is maintained by their continuous precipitation by means of barium chloride.

Decomposition voltage

The theoretical decomposition voltage of chlorides can be calculated from the value of equilibrium oxidation potential of the chlorine electrode $\varepsilon_{Pt,\,Cl_2\,|\,Cl^-}$ in the anolyte and the reversible reduction potential of the hydrogen electrode $\pi_{OH^-\,|\,H_2,\,Pt}$ in alkaline catholyte. If we apply the Nernst equations for the corresponding electrochemical processes [see (XI-9) and (XI-10)] we obtain the

following equations for individual mentioned potentials at 25 °C temperature and 1 atm. pressure of hydrogen or chlorine:

$$\varepsilon_{Pt,Cl_2 \mid Cl^-} = -1.358 + 0.05915 \log a_{Cl^-}, \qquad \text{(XI-16)}$$

$$\pi_{OH^- \mid H_2, Pt} = -0.828 - 0.05915 \log a_{OH^-} \qquad \text{(XI-17)}$$

Decomposition voltage is usually calculated under the assumption of a catholyte with unit activity of hydroxyl ions ($a_{OH^-} = 1$) and anolyte with unit activity of chloride ions ($a_{Cl^-} = 1$). Under these conditions the reversible decomposition voltage of an alkali chloride can be determined by the following equation:

$$(E_R)_t = -E'_{min} = -(\varepsilon_{Pt,Cl_2 \mid Cl^-} + \pi_{OH^- \mid H_2, Pt}) = -(-1.358 - 0.828) = 2.186 \text{ V}. \qquad \text{(XI-18)}$$

If electrolysis is carried out in a "batch process" using electrolytic cells with nonfiltrating diaphragms the caustic concentration in the catholyte increases and the chloride concentration in both anolyte and catholyte decreases. This change in composition is accompanied by a change in the theoretical decomposition voltage. If electrolyzers with flowing electrolyte and filtering diaphragms are used stationary conditions will be achieved and the composition of the electrolyte will remain constant in the vicinity of both anode and cathode. When making an exact determination of theoretical decomposition voltage the actual values of the activity of hydroxyl ions and chloride ions in the electrolyte must be taken into account. Under operating conditions there are on the average 100 grams of sodium hydroxide and 190 grams of sodium chloride per 1 litre of solution in the vicinity of the cathode and 265 grams of sodium chloride per 1 litre of solution in the proximity of the anode. These data will now be used to determine the potential at the anode and the cathode assuming an operating temperature of 25 °C.

An anolyte containing 265 grams of NaCl per litre has 5.026 moles of NaCl in 1000 grams of water (i. e. $m_{Na^+} = m_{Cl^-} = 5.026$). In the Table 8 it will be seen that the mean activity coefficient of sodium chloride in this solution $\gamma_{\pm}$ equals 0.877. This value will be further considered to coincide with the activity coefficient of chloride ions (γ_{Cl^-}) in a solution of the same concentration. The potential of the chlorine electrode then equals:

$$\begin{aligned} \varepsilon_{Pt,Cl_2 \mid Cl^-} &= -1.358 + 0.05915 \log a_{Cl^-} = \\ &= -1.358 + 0.05915 \log m_{Cl^-}\gamma_{Cl^-} = \\ &= -1.358 + 0.05915 \log 5.026 \,.\, 0.877 = -1.320 \text{ V}. \end{aligned}$$

In a catholyte containing 100 g NaOH and 190 g NaCl per litre of solution there are 2.73 moles of NaOH and 3.55 moles of NaCl in 1000 grams of water (i. e. $m_{Na^+} = 6.28$, $m_{Cl^-} = 3.55$ and $m_{OH^-} = 2.73$). In order to calculate the activity coefficient of sodium hydroxide or of hydroxyl ions respectively the Debye-Hückel theory is applied; according to this, the activity coefficient of

a given electrolyte is the same in all solutions possessing the same ionic strength [see equations (V-58) and (V-59)]. The ionic strength expressed in molality of a given solution with ions of univalent type will then equal:

$$\mu = \tfrac{1}{2}\,(m_{Na^+} + m_{Cl^-} + m_{OH^-}) = 6.28.$$

It will be found in the Table 8 that the mean activity coefficient of NaOH or rather the activity coefficient of hydroxyl ions in solutions of pure sodium hydroxide with an ionic strength $\mu = 6.28$ (equal to the value of the molality, in this case) will be:

$$\gamma_{\pm} = \gamma_{OH^-} = 1.37.$$

An activity coefficient of the same value may be assumed to hold good for the mixed solution under examination. The potential of the hydrogen electrode then equals:

$$\begin{aligned}\pi_{OH^-\,|\,H_2,\,Pt} &= -0.828 - 0.05915 \log a_{OH^-} = \\ &= -0.828 - 0.05915 \log m_{OH^-}\,\gamma_{OH^-} = \\ &= -0.828 - 0.05915 \log 2.73 \times 1.37 = -0.862 \text{ V}.\end{aligned}$$

The resultant decomposition voltage has then the following value for concentrations used in industry:

$$(E_R)_t = -E'_{min} = -(-1.320 - 0.862) = 2.182 \text{ V}. \qquad \text{(XI-18a)}$$

If we compare this value with that one resulting from equation (XI-18) it will be seen that they both are the same. Hence it is clear that the composition of an electrolyte has almost no influence on the value of the decomposition voltage within the limits of concentrations discussed.

The operating voltage applied to an electrolytic cell working at a given current load exceeds the theoretical decomposition voltage partly by the value of the polarization voltage, partly by the value of the voltage necessary to overcome various ohmic resistances. No account need be taken of the diffusion potential between the anolyte and the catholyte because it is of negligible value.

Regarding polarization voltages, the most important is the overvoltage at which both gases are liberated at the anode and the cathode and which increases with increasing current density and decreasing temperature. Its magnitude also depends to a large extent upon the material of the electrodes. In this respect iron is the best material for cathodes and graphite for anodes. Electrolysis is then effected at an increased temperature of about 70 to 80 °C which exerts a favourable influence as it lowers overvoltage and the ohmic resistance of the electrolyte. (Electrolysis in bell-jar type electrolyzers is an exceptional case where the temperature must not exceed 35 °C; failing this, thermally induced motion will disturb the natural stratification of anolyte and catholyte.)

Ohmic resistances such as, resistance of the electrolyte, the diaphragm, the electrodes and electric conductors must also be taken into account.

The voltage necessary to overcome resistance of the electrolyte is proportional to the current density, the distance between electrodes and the specific resistance of the solution. Resistance of an electrolyte decreases with increasing temperature. A small amount of chlorine bubbles in the anolyte will have no noticeable influence upon the resistance.

The resistance of a diaphragm increases with age. At a current density of 8 A/sq. dm and a temperature of 75 °C an asbestos diaphragm of 1.3 mm thick has an electric resistance which can be overcome by 0.12 to 0.15 V.

The distribution of the voltage across the electrolytic cell of the Vorce design operating under 10 A/sq.dm current density during electrolysis of a solution of common salt is given in the following table:

	Maximum	Minimum
Cathode potential (including overvoltage)	1.260	1.160
Anode potential (including overvoltage)	1.685	1.610
Voltage drop in the electrolyte	0.403	0.403
Voltage drop in the diaphragm	0.145	0.145
Voltage drop in the anode	0.100	0.100
Voltage drop in the conductors	0.100	0.100
Total	3.693 V	3.518 V

Other diaphragm processes require more or less the same voltage, i. e. 3.6 to 3.8 V across the bath when graphite anodes are used. With magnetite anodes the operating voltage amounts 4.4 to 4.6 V because of the higher chlorine overvoltage and the greater resistance of the material.

Energy consumption

The amount of energy consumed depends upon the voltage across the bath and the current efficiency of the electrolytical process. Although three products alkali hydroxide, chlorine, and hydrogen are obtained when electrolyzing a solution of sodium or potassium chloride, current efficiency is usually assessed by the resultant caustic which is the main product.

According to Faraday's law, 1 ampere-hour of current consumed in the electrolysis of sodium chloride should yield 1.492 grams of sodium hydroxide, 1.323 grams of chlorine and 0.0376 grams of hydrogen; thus 67 kiloampere-hours are theoretically required to produce 100 kilograms of hydroxide. If we assume the reversible decomposition potential of sodium chloride to be 2.186 V under the above conditions, then we can calculate theoretically from the following equation the energy required to produce 100 kilograms of caustic:

$$W_t = 2.186 \times 67 = 146.5 \text{ kwh} \qquad \text{(XI-19)}$$

If the operating voltage across the bath equals E volts and the current ef-

ficiency equals η_I (per cent) then the actual consumption of current necessary to produce 100 kilograms of NaOH equals:

$$W_s = 6\,700\,\frac{E}{\eta_I}\ \text{kwh.} \qquad \text{(XI-20)}$$

The ratio of values W_t and W_s in percents indicates the total energy (power) efficiency of the electrolysis. The efficiency of the production of potassium hydroxide is calculated analogously.

β. Design of electrolyzer with iron cathode

We have already learnt in the theoretical section of this book that for electrolysis to proceed advantageously it is necessary to prevent hydroxyl ions being transported from the cathode to the anode. This will be achieved by a diaphragm, if the electrolyte is stationary, or by stratifying the anolyte and the catholyte. This is made possible by their different respective densities while allowing a slow motion of the electrolyte from the anode toward the cathode. Finally this result can be achieved by separating the anodic and cathodic space by a diaphragm through which the electrolyte is allowed to flow from the anode toward the cathode at a slow rate. According to the method by which the anolyte and catholyte are separated we discern electrolytic vessels as follows:

electrolyzers with a nonfiltering diaphragm;

bel-jar type electrolyzers;

electrolyzers with a horizontal or vertical filtering diaphragm.

Before dealing in more detail with the design of individual types let us consider the basic requirements for electrodes and diaphragms.

A cathode on which hydrogen is deposited from a solution of sodium or potassium hydroxide is made of iron as hydrogen overvoltage with iron is much less than with other alternative metals (such as lead, copper, nickel etc.). Electrolyzers with nonfiltering diaphragm have cathodes of unperforated sheets while electrolyzers with filtering diaphragm have suitably perforated cathodes or iron gauze cathodes to allow the flow of the electrolyte.

The anode should withstand the corrosive effect of wet chlorine, oxygen, hydrochloric acid and hypochlorous acid. Apart from this, it should have a chlorine overvoltage as low as possible, good electrical conductivity and sufficient mechanical strength. Platinum, magnetite, carbon and graphite can be used as material. At a given current density and temperature the overvoltage on platinized platinum practically equals zero; a higher value has been observed with smooth platinum and graphite, while magnetite displays comparatively the highest overvoltage.

However, platinum which suits the purpose admirably owing to the excellent resistance against corrosive substances cannot be used nowadays because of the prohibitive price. Magnetite electrodes although quite satisfactory as far as chemical stability is concerned, possess poor electrical conductance and are

moreover rather fragile. Carbon electrodes have low resistance against the anodically deposited oxygen and have comparatively poor electrical conductance. The only material which meets all requirements fairly well is graphite; so nowadays it is exclusively used for the construction of anodes. Its disadvantage is that it is porous which limits its durability because the electrolyte filling the pores is also electrolytically decomposed and the brine confined within the pores cannot be easily replaced. In this way chloride very quickly becomes depleted which results in an increased discharge of hydroxyl ions and the liberation of oxygen. The evolution of oxygen is also promoted by the fact that there is a lower potential within the pores of the electrode than on the surface; this has been proved experimentally. Under these conditions a greater amount of hydroxyl ions than chlorine ions is discharged within the pores because the potential-current curve of chlorine decreases rapidly with a diminishing electrode potential while the drop in the corresponding curve for oxygen is relatively small within the considered range of potentials. The oxidation, making carbon to carbon dioxide by the liberated oxygen, results in an increased porosity of graphite whereby its mechanical cohesion is impaired to such an extent that small particles break off and the electrode begins to disintegrate. The destruction of graphite is further increased by high temperatures (by which the rate of carbon oxidation increases while oxygen overvoltage decreases) and considerably high current densities. To remedy this it was contemplated to impregnate the electrodes with various substances. Results, however, proved unsatisfactory as impregnated electrodes require a higher voltage and very easily crack when immersed in a bath. For this reason only graphite stems which lead the current to the anodes are sometimes impregnated. This prevents the electrolyte creeping and corrosion of the copper sleeves of the electrodes.

Diaphragms which separate the anolyte from the catholyte are distinguished as filtering diaphragms and nonfiltering diaphragms.

Nonfiltering diaphragms which are used to prevent diffusion and the mechanical mixing of the anolyte and the catholyte should possess a high diffusion resistance and a low electrical resistance (i. e. they should allow the easy passage of ions); they should also withstand the effects of both alkaline catholyte and acid anolyte. Electrolyzers used for production of caustic have diaphragms made of cement. To attain the desired degree of porosity a solution of common salt is added to the cement mixture; after the cement has set, salt crystals will be formed. After further treatment with water, salt will dissolve and leave fine pores in the cement. Diaphragms must have a satisfactory mechanical strength and, therefore, they are made rather thick (10 to 20 millimeters) and reinforced with thin iron wire netting which is placed into the cement before it sets. Cement does not indefinitely withstand the effect of electrolyte so a diaphragm will deteriorate after a certain period of time and must be replaced after 1 to 2 years. During electrolysis the pores of the diaphragm become clogged with different solid impurities which increases electrical resistance.

Filtering diaphragm prevents caustic penetrating from the cathode to the

anode by allowing the electrolyte to flow continuously from the anode to the cathode, i. e. in the direction opposite to the migration of hydroxyl ions. This type of diaphragm must have low electrical resistance, sufficient mechanical strength, chemical stability against corrosion and allow the electrolyte to be filtered at a certain velocity. There are no special requirements with regard to the magnitude of the diffusion resistance.

Asbestos is the only material used for the manufacture of filtering diaphragms which are made in the form of plates, cloth or paper. The diaphragm should be permeable enough to allow a concentration of 100 to 140 grams of NaOH per litre electrolyte to be attained per pass when operating at a normal current density. The permeability of a new diaphragm is three to five times higher than required, but after 2 to 10 days the permeability decreases to the degree needed. When wet it possess low mechanical strength and must be handled with care. To keep permeability normal all mechanical impurities as well as salts of calcium and magnesium must be removed from the electrolyte.

Electrolyzer with nonfiltering diaphragm

As previously stated, is the transport of electricity through the diaphragm in the first stages of electrolysis, when the concentration of alkali chloride is high and that of the caustic formed low, mediated by the ions of alkali metal which migrate towards the cathode and by the chloride ions migrating towards the anode. Under these conditions the diaphragm is able to retain in the catholyte all caustic formed. As concentration of caustic will increase during electrolysis the hydroxyl ions will transport more and more current, while the portion transported by chloride ions will steadily decrease. It is obvious that the diaphragm does not prevent the migration of hydroxyl ions.

As the transport of hydroxyl ions into the anode compartment causes a loss of caustic, current efficiency is also diminished during extended electrolysis in proportion to the increasing concentration of the caustic formed. The dependence of current efficiency upon the momentary concentration of caustic can be deduced from the theory according to which in the presence of several kinds of ions of the same polarity the individual ions take part in the transport of current in proportion of their specific conductivities. This can be expressed by the equation:

$$\frac{\varkappa_1}{\varkappa_2} = \frac{1-x}{x} \qquad \text{(XI-21)}$$

Here $\varkappa_1$ and $\varkappa_2$ stand for the respective specific conductivity of chloride and hydroxide of an alkali metal, x stands for the part of current transported toward the anode by caustic and $(1-x)$ for the part of current transported by the chloride ions toward the same electrode.

If we assume that specific conductivities within the considered range of electrolyte composition are approximately in proportion to the concentration

of the corresponding chemical substances and that their values remain constant even in a mixed solution of salt and caustic, we may write that:

$$\varkappa_1 \cong k_1 c_1,$$

$$\varkappa_2 \cong k_2 c_2.$$

If we use these expressions in the equation (XI-21) the part of current transported by the caustic will be obtained:

$$x = \frac{1}{1 + \frac{k_1}{k_2} \frac{c_1}{c_2}} = \frac{1}{1 + k \frac{c_1}{c_2}} \qquad \text{(XI-22)}$$

From this equation it will be seen that during the initial stages of electrolysis ($c_2 \cong 0$) the transport of current is performed solely by the chloride of the alkali metal ($x = 0$). As previously mentioned the composition of the anolyte and the catholyte changes during electrolysis of sodium chloride. On passage of one Faraday's charge 1 gram-equivalent of NaOH is formed in the cathode compartment while only 0.6 gram-equivalent of Cl^- emigrates from the catholyte. Similar conditions are encountered during electrolysis of potassium chloride. During electrolysis migration takes place causing the concentration c_2 of caustic in the catholyte to increase more quickly than decreases the concentration c_1 of the salt. This results in a very quick decrease in the value of the fraction c_1/c_2 in the equation (XI-22) as electrolysis proceeds whereby x will duly increase.

It will be demonstrated that current efficiency also decreases with an increased concentration of the caustic. Should the transport of current be performed by hydroxide ions alone (the transference number of OH^- is t'_-), the formation of 1 gram-equivalent of hydroxide would be accompanied by the simultaneous emigration of t'_- gram-equivalents of OH^- from the cathode compartment. Actually, however, only an x-th part of the current is transported by the caustic, thus merely ($t'_- \cdot x$) gram-equivalent of OH^- are transferred from the catholyte. The current efficiency η_I in per cent is, therefore, given by the equation:

$$\eta_I = 100\ (1 - t'_- \cdot x) \qquad \text{(XI-23)}$$

On substituting the term of the right half of the equation (XI-22) into the equation (XI-23) we obtain an equation which enables us to calculate the current efficiency at any time during electrolysis if the value of concentration ratio c_1/c_2 at the cathode side of the diaphragm is known:

$$\eta_I = 100 \left[1 - \frac{t'_-}{1 + k \cdot \frac{c_1}{c_2}} \right] \qquad \text{(XI-24)}$$

This equation indicates that during the first stages of electrolysis, when the concentration of caustics is still negligible ($c_2 \cong 0$), current efficiency equals 100 per cent. In the course of time, however, current efficiency steadily decreases and after a longer period, when the concentration of chloride drops to zero ($c_1 \cong 0$), it theoretically attains the limit value $\eta_I = 100\ (1 - t'_-)$. This theoretical result is confirmed in the table below which shows the experimental results obtained on the electrolysis of potassium chloride.

Period of electrolysis, in hours	Average current efficiency (in per cent) within the periods considered	c_1	c_2	Efficiency at the end of a period as calculated from equation (XI—24) (in per cent)
		equivalents in 100 ml		
0—2	88.06	0.2382	0.0418	81.3
2—4	75.30	0.2224	0.0754	70 4
4—6	66.50	0.2096	0.1071	62.6
6—8	58.02	0.2066	0.1331	55.0

From this it can be seen that there is a clear correlation between the average efficiencies experimentally determined by analysis of samples drawn at certain intervals during electrolysis and the momentary efficiencies at the end of each period which have been calculated from equation (XI-24). The efficiencies calculated are somewhat lower than the experimental data, which agrees with the fact that efficiencies are calculated at the ends of the periods when the concentration c_2 is higher than the average concentration during the period under observation. It is evident from what has been said before, that satisfactory efficiency can only be attained if a permanent excess of chloride is maintained in the electrolyte. Therefore, the diaphragm method is not suitable for the production of concentrated caustic solutions because efficiency may become uneconomically low and also the total conversion of chlorine into hydroxide is not possible. This process only yields diluted solutions of caustics which are rich in chloride; after electrolysis they are concentrated by evaporation and the salt (NaCl or KCl) separated from them by crystallisation is returned to the process.

The chlorine yield is naturally below 100 per cent, too, because the hydroxyl ions migrating into the anolyte react with it and give hypochlorite and chlorate [see equations (XI-13) and (XI-14)]. Apart from this, chlorine contains a certain amount of oxygen and carbon dioxide resulting from secondary reactions; the content of these gases in the anode gas depends on the quantity of hydroxyl ions migrating from the catholyte to the anolyte, i. e. on the height of the concentration of caustic in the catholyte. Consequently, the alkali hydroxide solution produced by electrolysis must not exceed a certain maximum concentration if we take into consideration the desired hydroxide yield, the purity of chlorine and the durability of the graphite anodes.

As the transference number of the OH-ions formed by dissociation of potassium hydroxide is lower than that of sodium hydroxide*) it is obvious from equation (XI-24) that the yields obtained on electrolysis of potassium chloride

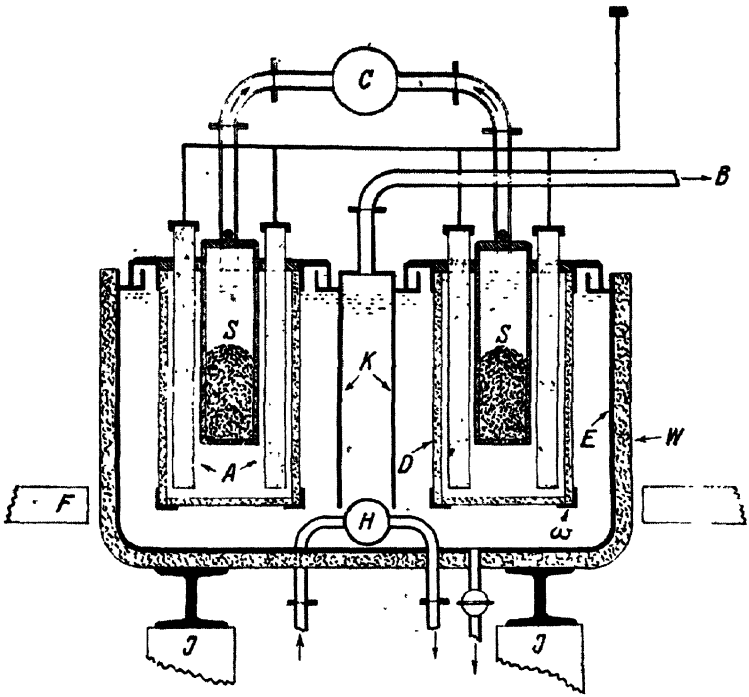


Fig. 83. The Griesheim-Electron Comp. electrolyzer (side elevation).
A — Graphite anodes suspended in anode box, *B* — Hydrogen outlet, *C* — Chlorine outlet, *D* — Cement diaphragms, *E* — Iron electrolyzer tank, *H* — Steam heating, *K* — Cathodes, *S* — Stoneware perforated cylinder containing solid sodium chloride, *W* — Thermal insulation of diatomaceous earth (kieselguhr), *w* — Angle irons of the frame.

under the same conditions will exceed those obtained on electrolysis of sodium chloride. This assumption agrees with practical results.

The transference number of hydroxyl ions decreases with increased temperature and approaches the value of 0.5. According to equation (XI-24) increasing

*) For example at a concentration of 1 gram-equivalent of KOH or NaOH per 1 litre of solution and at a temperature of 18 °C the transference number of OH^- (i. e. t_-) equals 0.74 for potassium hydroxide and 0.82 for sodium hydroxide.

temperature will improve the current efficiency of electrolysis which agrees with practical experience.

The equation (XI-24) is valid only approximately as it was derived on the assumption of a direct proportionality between the conductance and concentration of individual single components, while the influence of the composition of the solution upon the transference number of hydroxyl ions was neglected. Apart from this, no account at all was taken of the diffusion of caustic from catholyte to anolyte or of the fact that caustic and salt concentration in close

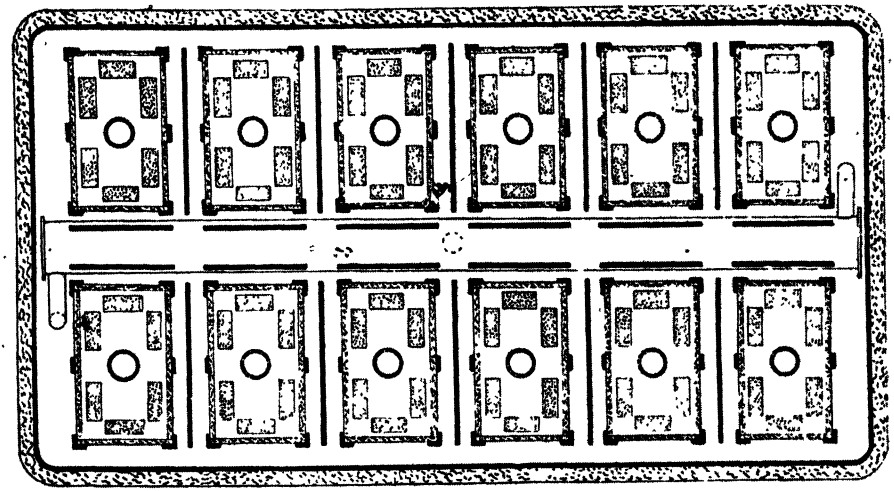


Fig. 84. The Griesheim-Electron Comp. electrolyzer (top view).

proximity of the diaphragm, which is decisive for the transfer of the ions between the anolyte and the catholyte, is not the same as in the bulk of catholyte, wherefrom analytical samples are drawn. Actually the concentration of OH^- ions is highest at the cathode and decreases towards the diaphragm; therefore the transport of the negative current close to the cathode is carried out solely by hydroxyl ions; with an increased distance from the cathode the chloride ions transport more and more current and are finally the only current carriers through and beyond the diaphragm, i. e. in the anode compartment (provided no OH^- ions penetrated here from the catholyte). The transport of current in the close proximity of the anode is also performed to a small extent by hypochlorite ions. The positive current in the electrolyte is carried almost exclusively by Na^+ ions while nearer the anode hydrogen ions play also a part.

The electrolyzer of the *Griesheim Electron Company* is one of the original electrolyzers with nonfiltering diaphragm (Figs. 83 and 84).

Although this type of electrolyzer is now a thing of past, it is still interesting as modern electrolyzers after various improvements were derived from it. The main part was an iron tank *E* about 4800 mm long, 3800 mm wide and some 1200 mm high. It was thermally insulated on the outside by a layer of kieselguhr *W*. The bottom had a drainage pipe and a cock for the discharge of the produced caustic solution. The inner walls of the tank as well as the inserted plates *K* which did not quite reach to the bottom of the tank served as cathodes. At the same time the iron plates divided the space of the tank into 12 compartments into which the anode boxes 1100 mm long, 750 mm wide and 1000 mm high were suspended. The side walls of the anode box were made of cement diaphragms *D* roughly 10 mm thick which were inserted into frame *w* made of angle iron. The bottom of the chamber was a steel sheet; all splits were carefully filled with cement and all the iron parts were similarly protected against the corrosive effect of chlorine. The top of each box was sealed by a concrete cover which had six carbon anodes *A* passing through it. They were roughly 600 mm high, 300 mm wide and 70 mm thick; anodes were placed near the walls of the box. In this way there was an anode at the inner side of the diaphragm and a cathode at the outer side. Between the anodes was a stoneware cylinder *S* perforated in the lower part. The cylinder was filled with sodium or potassium chloride which gradually dissolved in the anolyte so that the electrolyte was always saturated. The whole tank of 12 anode boxes was covered by an iron plate, bent at the edges, which was dipped into a liquid seal. The hydrogen which accumulated under these covers was taken off through piping *B* while chlorine was drawn off through tube *C*.

When the operation started, the iron tank and the individual boxes were filled with saturated solution of sodium (or potassium) chloride while solid salt was put into the stoneware cylinders. The level of electrolyte in the anode boxes was always somewhat higher than in the tank. During electrolysis the temperature was kept at 85 °C by steam heating; steam entered the heating element of the tank through piping *H*. The voltage across the electrolyzer was 3.5 to 4.0 V. The total current load was about 2500 A which corresponded to a current density of some 2 A/sq. dm.

Electrolysis was maintained by a gradual replacement of the salt consumed till the concentration of the catholyte attained 40 to 50 grams of NaOH, apart from the remaining 260 g of NaCl in one litre of the solution; on electrolyzing potassium chloride a higher concentration was attained, about 70 to 80 grams of KOH, apart from the remaining 200 grams of KCl per litre of solution. When this concentration was reached the current was switched off and the caustic was drained; after refilling the tank with fresh brine the cycle restarted. One operating period took about 3 days.

The concentration of caustic solution produced was very low and also current efficiency was very small, between 75 and 80 per cent. This was due to the migration of hydroxyl ions from the catholyte to the anolyte which gave rise to hypochlorite ions. These were then anodically oxidized to chlorate ions under

simultaneous evolution of oxygen which oxidized the carbon of the electrodes. The anode gas escaping from the electrolyzer often contained up to 12 per cent carbon dioxide and 5 per cent oxygen. In these conditions the durability of the anodes was very limited, which means that they had to be replaced every four to six months.

Other difficulties were caused by the high content of carbon dioxide in chlorine. This resulted in an inferior product when such a chlorine was used for production of bleaching powder. Griesheim Co. tried to overcome this drawback by using magnetité electrodes. These were an improvement indeed, and it was possible to obtain chlorine quite free of carbon dioxide, however, the voltage across the electrolyzer rose from 3.5—4 V to 4.4—4.6 V, owing to a higher chlorine overvoltage at the anode.

Bell-jar type electrolyzers

Original electrolyzers with nonfiltering diaphragm had a drawback because at a higher caustic concentration it was impossible to prevent the penetration of hydroxyl ions into the anode section. With bell-jar type electrolyzer, which appeared later, this problem was solved by allowing the electrolyte to flow at a certain velocity from the anode to cathode so that it left the zone of electrolysis before the hydroxyl ions were able to reach the anolyte by migration and diffusion. In this case the direction of flow of the brine through the electrolyzer was opposite to that of the migration of the hydroxyl ions towards the anode.

The unit consisted of a tank into which an inverted non-conducting bell-jar dipped which was closed at the top and fitted with an inner graphite anode. The outer side of the bell was surrounded with an iron ring acting as the cathode. The brine was continually fed into the bell, became enriched by caustic and due to its increasing specific gravity it dropped to the bottom of the tank from where it was drawn off.

In difference to electrolyzers with nonfiltering diaphragm, a stationary state is attained with this type of electrolyzer after some time if the current load and the rate of flow of the brine is maintained constant. Under these conditions the composition of individual horizontal layers of electrolyte and the current efficiency during the electrolysis remain unchanged. Inside the bell-jar a sharp boundary can be discerned at a certain distance from the anode which separates as a neutral zone of the electrolyte the acid anolyte from the alkaline catholyte. If electrolysis takes place in a glass apparatus the boundary can be obviously seen because the impurities from the graphite are first dissolved in the acid anolyte and coming in contact with the alkaline catholyte are precipitated and so form a somewhat turbid zone.

The mutual mechanical mixing of anolyte and catholyte in the bell-jar type electrolyzer is prevented by stratification of the electrolyte due to difference in specific gravity of both liquids, so that no diaphragm is necessary. Simultaneously the motion of the electrolyte from the anode toward the cathode prevents the penetration of hydroxyl ions towards the anode which enables to attain

a higher current efficiency as well as a higher concentration of caustic solution. At a given current density, which is very limited with this type of electrolyzer (see later), the concentration of hydroxide in the solution produced depends upon the rate of the flow of brine. Obviously the concentration of the caustic solution will increase with a slower flow of brine.

The current efficiency at a given current density is influenced by the rate of flow in the following manner. A very slow flow does not prevent the hydroxyl ions from penetrating the anolyte, so that the resultant current efficiency is not satisfactory and the product obtained contains a certain amount of chlorate. As the rate of flow of electrolyte increases the efficiency gradually rises according to the decrease in the number of hydroxyl ions transported to the anode, till it attains the maximum when the velocity of flow equals the velocity at which the hydroxyl ions are transferred to the anode by migration and diffusion. If the rate of flow is increased still further the current efficiencies will be lowered again because the brine carries a large quantity of dissolved chlorine from the anolyte to the catholyte thus causing by formation of hypochlorite a drop in the amount of the caustic solution produced.

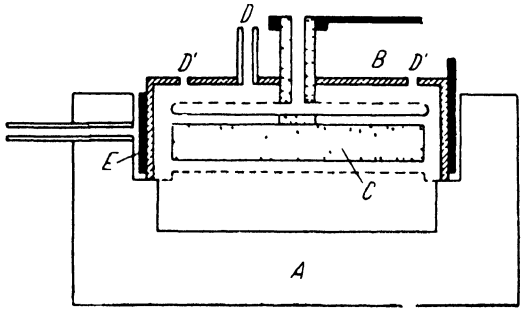


Fig. 85. Bell-jar type electrolyzer (sectional view).

A — Concrete tank, *B* — Bell-jar, *C* — Graphite anode *D* — Chlorine outlet, *D'* — Opening for connection o gas spaces of two adjacent bell-jars, *E* — Iron cathode.

Therefore the correct setting and maintaining of the rate of flow of the brine is of great importance. To prevent a disturbance of natural stratification of the electrolyte by thermal convection the operating temperature of the electrolyzer should not exceed roughly 35 °C. In order to reduce the solubility of chlorine in the electrolyte it is necessary to keep a high chloride content in the brine.

On the whole it may be stated that due to the fact that hydroxyl ions are removed from the reaction zone before they can react with chlorine, more concentrated caustic solutions are here obtained than with electrolyzers using nonfiltering diaphragms. In spite of this improvement it is not possible to convert all chloride into hydroxide should be a satisfactory current efficiency attained and a caustic with a low content of hypochlorite and chlorate produced.

A bell-jar type electrolyzer was designed by the Czechoslovak Society for Chemical and Metallurgical production, Ústí n/L., Czechoslovakia (see Fig. 85 and 86).

This electrolyzer consists of a concrete tank A, 2500 to 3000 mm in length and 1250 mm in width. The top recess of the tank walls supports 21 to 25 bell-jars B. These bell-jars are made of concrete in the form of inverted troughs which are open at the bottom. Stems which carry current to anodes C are inserted through a central opening in each bell B while side opening D allows the chlorine produced to be taken off by a collecting pipe. U-shaped tubes are connected to openings D'; these tubes interconnect the gas spaces of all bells in

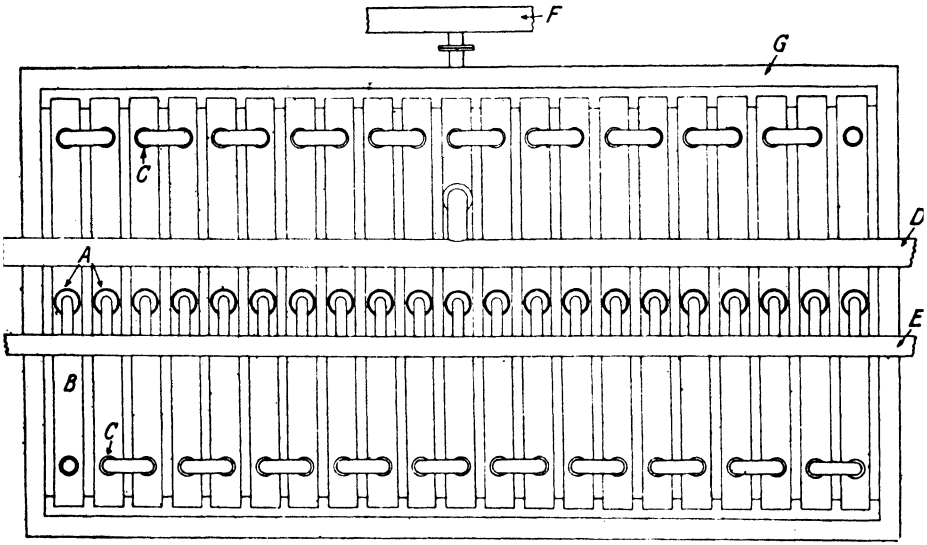


Fig. 86. Bell-jar type electrolyzer (top view).
A — Brine inlet, *B* — Bell-jars, *C* — Pipes interconnecting individual bells, *D* — Chlorine outlet, *E* — Main brine feed pipe, *F* — Caustic solution drain, *G* — Concrete tank.

order to prevent the fluctuation of pressure over the liquids and to maintain the existing stratification of electrolyte. The outside of the bells is surrounded by belt-shaped iron cathodes E which are connected to the negative pole of the source of current. Inside the bell a horizontal graphite plate C takes up nearly the whole cross section of the bell and acts as an anode; small holes in the plate facilitate the escaping of chlorine; current is led in from the mains by a graphite stem. All the plates in the bells are connected in parallel to the positive pole of a rectifier. Fresh brine is either led through a duct bored in the graphite stem or through a separate inlet tube at the side of the stems; this inlet is connected to a horizontally arranged glass tube having holes in the top which permit a uniform distribution of the brine in the electrolyzer. The neutral zone between the anolyte and the catholyte is 20 to 25 mm underneath the anode.

The caustic solution produced accumulates on the bottom of the tanks and is drained away through a side opening. Hydrogen is usually not collected.

Great care must be taken to ensure a regular inlet and a correct distribution of fresh brine throughout the entire cross section of the bell in order to maintain a correct functioning of the electrolyzer. Failing this, the neutral zone would be disturbed and current efficiency would decrease. The brine inlet, therefore, has an automatic controller. To prevent the anolyte and catholyte mixing thermally, a comparatively low temperature of 30 to 35 °C is to be maintained. This design of electrolyzer has rather a great distance between the electrodes, so higher voltage is necessary to overcome the resistance of the electrolyte; for this reason current density of comparatively very low value is to be used, some 3 amperes per square decimeter of the bell cross section (a total of 25 amperes per one bell), so as to prevent the electrolyte being heated through the liberation of Joule's heat above the permissible limit.

The alkali hydroxide solution produced in this electrolyzer had a concentration of 110 to 130 grams of NaOH per litre and the average current efficiency amounted to 88 per cent. The voltage across the bath fluctuated between 3.7 and 4.2 V.

Although the design of the above-mentioned type of electrolyzer was on the whole a successful way to produce continuously caustic without the use of a diaphragm, too much floor space was taken up by the electrolyzer owing to the comparatively low current density. A considerable number of these units ought to be installed to obtain the capacity required. This is the reason why the bell-jar type electrolyzer had not been widely used. Actually, electrolyzers with filtering diaphragms were already being used in the industry at that time (1905 and 1910) having produced caustic in a more concentrated solution at a lower current consumption.

In the *Billiter-Leykam* modification of the bell-jar type electrolyzer (see Fig. 87) are the electrodes placed more closely together. The voltage across the cell is lowered by the use of special asbestos membrane which permits to draw off the hydrogen from the cathode space.

The iron tank of the electrolyzer *1* (2000 × 1910 × 470 mm) was lined with ceramic tiles and divided by partitions *2* and *3* into four compartments. Partition *2* reached half-way up the electrolyzer and supported the graphite anodes *4*. Partition *3* reached the upper edge of the tank and supported covers *5*. Cathodes *6* of T-shaped bars were enveloped by asbestos membrane *7* which served to take off the hydrogen; the membrane was reinforced by an asbestos-cement plate which kept the membrane taut and allowed an easy passage of the hydrogen. One end of the membrane together with the cathode bars was inserted into partition *3* and the other end into the opposite wall of the electrolyzer. The membranes ran into the adjacent hydrogen chamber and were arranged slightly inclined to ease the hydrogen escaping. There were 20 cathodes in each compartment, i. e. 80 cathodes in the whole electrolyzer. All cathodes were connected to the negative pole of the source of current by conductor *13*. Hydrogen from

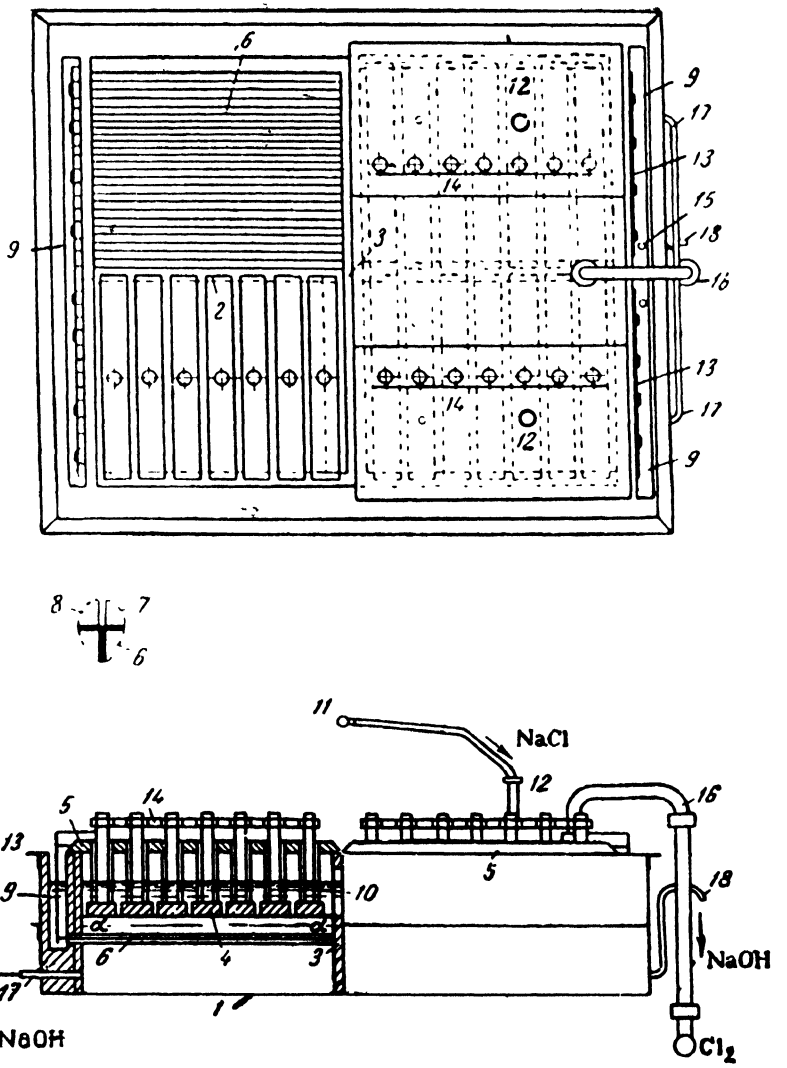


Fig. 87. The Billiter-Leykam electrolyzer

1 — Electrolyzer vessel, *2*, *3* — Partitions, *4* — Graphite anodes, *5* — Electrolyzer cover, *6* — Iron cathodes, *7* — Asbestos membrane, *8* — Membrane reinforcement (asbestos-cement plates), *9* — Hydrogen chamber, *10* — Insulating ceramic sockets, *11* — Brine feed pipe, *12* — Brine distributing pipes inside of the electrolyzer, *13* — Current connection (negative pole), *14* — Current connection (positive pole), *15* — Hydrogen take off pipe, *16* — Chlorine take off pipe, *17* — Caustic solution drain, *18* — Caustic solution drain, α—α — Position of the neutral zone.

side chamber *9* was taken off through holes *15* in the covers of the chambers.

The covers were traversed by graphite stems (insulated with ceramic sockets *10*) which were screwed into horizontal graphite plates *4*. At the top of the stems were sleeves to which the source of current was connected. Brine was fed into the tank through piping *11* and distributed through tubes *12* to four places under the covers. A still more even distribution was obtained if glass plates with a great number of small openings were placed onto the anodes. Chlorine accumulated under the covers was taken off through stoneware piping *16*.

The brine level was about 30 to 40 millimeters above the anode plates. The neutral zone was situated slightly above the membrane, near the line α—α. The caustic solution which accumulated at the bottom of the electrolyzer was drained away through piping *17*.

The electrolyzer could be fed by brine which had not been freed of calcium and magnesium salts yet the membrane did not get clogged by hydroxides of these metals as the caustic zone in which the precipitates were formed was situated above the membranes. Therefore, the precipitated hydroxides slid along the outer side of the membrane, fell to the bottom of the electrolyzer and were periodically removed.

Electrolyzers with membranes permitting an easy passage of current had an advantage over the bell-type electrolyzers because the electrodes could be set closer together so that a somewhat higher current density could be used. Apart from this, the electrolyzer was of simple design; attendance and operational control was easy so that one man per shift could be left in charge of the whole plant. One drawback, however, was the short service life of the membrane.

An electrolyzer of the above type was loaded with a current of 4000 amperes corresponding to the current density of roughly 5 A/sq dm at the anode. The voltage across the bath was 3.2 to 3.8 V at a temperature 45—60 °C Current efficiency attained 90 per cent while the content of sodium hydroxide in the caustic solution reached about 120 grams per litre.

Electrolyzers with horizontal or vertical filtering diaphragms

When using electrolyzers with horizontal filtering diaphragms the mixing of the catholyte with the anolyte is prevented both by stratification, according to their different densities, and by making use of diaphragms through which the electrolyte is allowed to pass from the anode to the cathode. The diaphragm — which in this case actually improves the principle of the bell-jar type electrolyzers — secures a more uniform operation, suppresses the effect of thermal convection (allows to work at a higher temperature which has a favourable effect as it lowers the voltage across the bath) and facilitates production of more concentrated caustic solutions with better current efficiency.

Since a diaphragm alone is sufficient for the mechanical separation of the anolyte and the catholyte, there are also electrolyzers with vertical filtering diaphragms through which the electrolyte passes at a certain velocity. An

electrolyzer vessel of this type is divided by a perforated cathode into cathodic and anodic compartment with a diaphragm of sufficient filtration capacity pressing against the cathode. The brine is fed into the anodic compartment where under hydrostatic pressure it flows through the diaphragm and comes into contact with the cathode at which the hydroxide is formed; the caustic solution flows through the holes in the cathode and sinks to the bottom of the cathodic compartment where it is continuously drained off the electrolyzer. In this case the electrolyte is not stratified according to the specific gravities of the layers but is divided by a diaphragm which has one side in contact with the acid anolyte and the other in contact with the caustic solution.

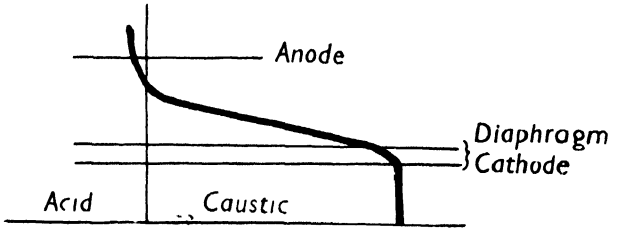


Fig. 88. Distribution of acid and caustic concentration in the proximity of a horizontal diaphragm

As well the bell-jar type electrolyzer as the cell just described work with a current efficiency which is dependent on the rate of flow of the brine at a given current density. If the flow is too fast the efficiency is low as excessive amounts of chlorine enter the cathode chamber and react with the alkali hydroxide A too low rate of flow exerts also a negative influence on current efficiency as the salt concentration in the brine considerably decreases and the concentration of caustic rapidly increases; this means that the hydroxyl ions migrate to the anode in greater quantities.

Apart from the rate of flow it is the current density which determines the rate of formation of caustic at the cathode, thus being an important factor in the electrolysis. It will be readily understood that with a given porosity of the diaphragm and a given rate of percolation the increased current density will increase the proportion of sodium chloride converted to caustic and vice versa. It has been experimentally established that current efficiency at first increases, then attains a maximum and finally drops when the current density is gradually raised. The explanation is simple. At very low current densities and a low rate of caustic formation results any small loss of caustic, caused by secondary reaction with chlorine, in a comparatively big loss of the total caustic formed and, consequently, in a marked lowering of the current efficiency. With a very high current density the concentration of caustic at the cathode is so increased that a larger part of the electricity will be carried by hydroxyl ions to the anode. The maximum current efficiency, therefore, will be at some inter-

mediate value. Assuming appropriate conditions have been adjusted, the current efficiency reaches 95 or 96 per cent. If not only a satisfactory current efficiency but also a high caustic concentration is desirable it is necessary to coordinate the current density and the rate of the percolation in order that the decomposition yield (i. e. the ratio of equivalents of hydroxide produced to the equivalents of salt entering the electrolysis) is as high as possible.

When using diaphragms there is no risk of the anolyte being mixed by thermal convection; so unlike the bell-jar electrolyzer higher temperatures may be used which lower the specific resistance of the electrolyte. The increased temperature has also a positive effect upon the current efficiencies as both, migration of hydroxyl ions from catholyte to anolyte and solubility of chlorine in brine, are reduced. By this, formation of hypochlorite is limited and caustic and chlorine losses are reduced.

In this case asbestos is the only suitable material for diaphragms being fully resistant against caustic while at least partially resistant against chlorine. Asbestos diaphragms are particularly suitable for electrolyzers with horizontal diaphragms as they are entirely surrounded by caustic solution (see Fig. 88). In such a medium the durability of asbestos is almost unlimited and the diaphragm requires replacement only after its permeability has been considerably impaired by precipitated hydroxides of alkaline-earth metals.

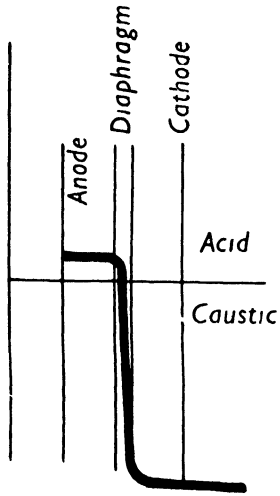


Fig. 89. Distribution of acid and caustic concentration in the proximity of a vertical diaphragm

Another advantage of electrolyzers with horizontal diaphragms is that there is no need to purify the brine too carefully as the impurities, namely Ca^{++} and Mg^{++} ions, are precipitated outside the diaphragm by the reaction with OH^- ions in the alkaline zone of the electrolyte before they can reach the diaphragm. The precipitates then fall onto the diaphragm forming a loose and fairly permeable layer which settles only after a longer period of time; then, of course, this layer is a hindrance to the free passage of electrolyte.

On the other hand a certain drawback of electrolyzers with a horizontal diaphragm is that their electrodes are working with one side only thus occupying a lot of floor space.

Units with vertical diaphragms are different from electrolyzers with horizontal diaphragms as the neutral zone is located in the centre of the diaphragm (see Fig. 89), thus the brine flowing through the electrolyzer comes in contact with the hydroxyl ions only in the pores of the diaphragm. If the

electrolyte contains calcium or magnesium ions a precipitate is formed which gradually fills the pores and rapidly impairs the permeability of the diaphragm.

The Siemens-Billiter electrolyzer is a notable representative of electrolyzers with a horizontal filtering diaphragm which is still used in some factories (see Fig. 90).

The electrolyzer *A* consists of a steel tank 5700 mm long, 4500 mm wide and 350 mm high. The inside walls are lined with a layer of cement which is sometimes covered with tiles. The cathode *C* is made of strong iron gauze and rests on supports which are welded to the bottom of the electrolyzer. Diaphragm *D* is placed on the cathode. The top of the electrolyzer is closed by a cover which is traversed by stems which lead the current to the electrodes. The distance between anode and cathode is 55 to 60 mm. Pipe *F* emerges from the cover and acts as a chlorine outlet. Hydrogen from the cathodic compartment passes through piping *G* and the caustic solution flows through the cathode gauze and is drained through tube *H*. Brine is led into the electrolyzer by a glass tube.

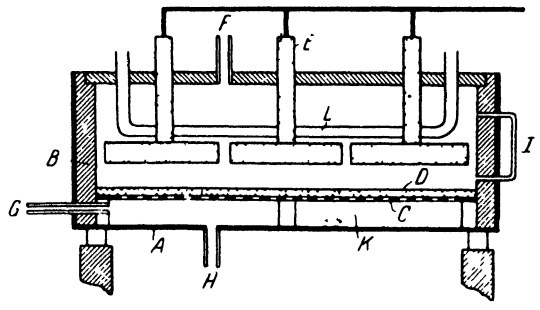


Fig. 90. Sectional view of a Siemens-Billiter electrolyzer with a horizontal filtering diaphragm

A — Iron tank, *B* — Cement lining, *C* — Iron wire-gauze cathode, *D* — Asbestos diaphragm, *E* — Graphite anodes, *F* — Chlorine outlet, *G* — Hydrogen outlet, *H* — Caustic drain, *I* — Level gauge, *K* — Space in which the percolated caustic solution is collected, *L* — Brine heater.

The diaphragm is prepared in the following way: First of all an asbestos cloth is placed on the cathode and the edges of it are attached with cement to the walls of the tank A paste made from asbestos, powdered baryte and brine is spread evenly over the cloth to a depth of 5 to 10 mm. After 5 to 6 hours the electrolyzer is cautiously filled with brine. A fresh prepared diaphragm is very permeable so that only diluted caustic solution can be produced; after about 15 to 20 days the permeability decreases and finally becomes constant. During this period while the diaphragm "forms" itself, the concentration of caustic solution increases and attains a final value of 12 to 16 per cent NaOH or 18 to 20 per cent KOH.

Today diaphragms consist of asbestos paper only the edges of which are fastened to the frame with putty made from barium sulphate and brine.

Although with this design the impurities contained in the brine (i. e. calcium and magnesium ions) are precipitated outside the diaphragm and fall on the diaphragm in the form of a loose and permeable sediment yet in the process the pores of the diaphragm become clogged after a longer time. This results in a rise in the voltage across the bath and a decrease in the energy efficiency.

In order to lengthen the service life of the diaphragm as much as possible the brine is chemically purified before it enters the electrolyzer, and apart from this the level of the brine is gradually raised during the process from 80 mm to 240 mm to increase the hydrostatic pressure on the diaphragm. When this measure proves ineffective the electrolyzer must be put out of operation and the diaphragm replaced by a new one.

The voltage across the bath depends on current density, e. g. at a density of 4.6 A/sq. dm of the anode area it is 3.7 V, at 7 A/sq. dm 4 V, and at 10 A/sq. dm 4.5 V. The voltage is, of course, lower at the beginning of the working cycle than at the end. At a sufficiently high current density the bath will be heated to the temperature required by Joule's heat while at a lower density the electrolyzer must be heated by a steam coil which is placed above the anodes. This prevents the thermal convection upsetting the spontaneous distribution of the electrolyte according to the specific gravity.

The advantage of an electrolyzer with a horizontal diaphragm is a high current efficiency at a relatively high concentration of caustic solution, a sufficiently long service life and an uninterrupted work. All this is a result of the diaphragm being arranged horizontally. The uniform hydrostatic pressure on the entire surface of the diaphragm ensures its uniform permeability. The diaphragm is less chemically attacked as it is entirely surrounded by caustic solution. Also, a spontaneous stratification of catholyte and anolyte is achieved so that in the vicinity of the anode the acid reaction of the brine is maintained which increases the durability of the electrodes as well as the current efficiency

Earlier types of electrolyzers worked with a current of 2200 A; the current density at the anode was 4.7 A/sq. dm and the voltage across the bath 3.7 to 4.2 V while the temperature of the electrolyte was 60 °C. The sodium hydroxide content in the caustic solution produced was about 120 grams per litre and the remaining sodium chloride amounted to some 180 grams per litre. Current efficiency was between 92 and 94 per cent.

In the modern type of electrolyzers the electrodes are set closer together: approximately 14—20 mm apart. The cathodes are corrugated and the anodes are shaped according to the corrugations. In this way it was possible to raise current density to some 15 A/sq. dm. In order to achieve the highest possible current efficiency a part of the electrolyte is continually removed from the electrolyzer, resaturated with sodium chloride and returned to the bath. The voltage across the electrolyzer amounts to 3.5 to 3.8 V. Electrolyzers for 12 000 to 24 000 A have been constructed for which less floor space was needed. These modern electrolyzers require 230 to 240 kw-hr. of direct current and 153 kg of NaCl to produce 100 kg of 100 per cent sodium hydroxide.

In spite of this, the Billiter electrolyzers still require much floor space; for this reason they use to be gradually replaced by compact electrolyzers with vertical filtering diaphragms.

The first electrolyzer of that type as seen in Fig. 91 was designed by *Hargreaves and Bird.*

This electrolyzer consisted of a high narrow frame with cement lining *Z*, diaphragms *D* and cathodes *K* made of copper gauze attached to the frame forming the side walls. The copper gauze supported the brittle diaphragms. The diaphragms and cathodes were placed between cement lined iron walls which were clamped together. The top of the electrolyzer had a cover to which a graphite rod carrying the graphite anode plates was fixed. The brine was led in by a pipe at the bottom of the electrolyzer. A part of the brine passed through the diaphragm and flowed as a diluted caustic solution to the outer cathodic compartments. The remainder of the electrolyte was led off from the anode compartment and resaturated with salt. In this way a high concentration of sodium chloride was maintained in the electrolyte. This was necessary for a satisfactory current efficiency. The diaphragms consisted of large plates about 3 to 4 mm thick made of a mixture of asbestos fibres, cement, chalk, and water glass.

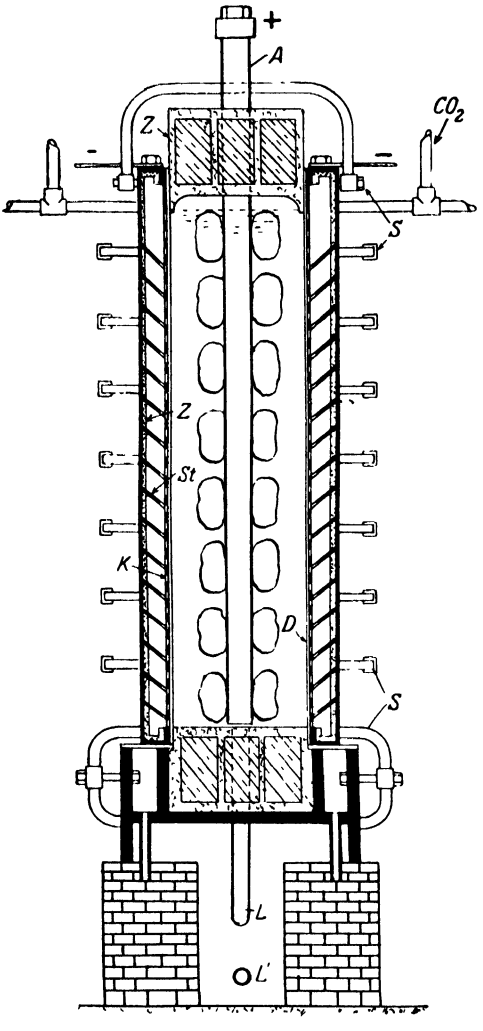


Fig. 91. Hargreaves-Bird electrolyzer:
A — Anode (from graphite plates), *B* — Diaphragm, *K* — Copper gauze cathode, *L* — Brine inlet, *L'* — Brine outlet (for saturation with salt), *S* — Fixing of electrode, *St* — Supports for diaphragm and cathode, *Z* — Cement lining of the frame.

As evident, only the central compartment of the electrolyzer described was filled with the electrolyte and the outer cathodic compartments were empty. Hence there was a difference in hydrostatic pressure alongside of the diaphragm which caused a higher rate of percolation at the bottom than at the top. On the other hand the current density was higher at the top of the electrode than at the bottom due to the proximity of the lead-in conductor. Hence, less electrolyte passed at a higher current density at the top of the

diaphragm and more electrolyte passed at a lower current density at the bottom which duly resulted in poor yields of the process. Inventors were aware of this deficiency and tried to overcome it by introducing carbon dioxide together with steam into the empty cathodic compartment. The hydroxide reacted with carbon dioxide to form carbonate whereby secondary reactions were suppressed to a certain extent for carbonate ions are much less mobile than hydroxyl ions. The steam increased the temperature and after condensation it washed the soda off down the cathodes. Although a higher current efficiency was reached, the product was lowpriced soda instead of more valuable sodium hydroxide.

The Hargreaves-Bird electrolyzer was loaded with 2600 A, current density on the surface of the diaphragm 2 A/sq. dm and voltage 3.6 to 4.0 V. 150 to 170 grams of sodium carbonate per one litre catholyte was obtained while currents efficiency was between 80 to 85 per cent. The temperature was maintained at about 80 °C.

This electrolyzer has not been used very much in its original design, yet it was the basis for a number of more modern designs.

De Nora's electrolyzer (Fig. 92) solves the problem of a nonuniform flow of the electrolyte through the diaphragm in the following way: On asbestos cardboard a paste is spread made of iron oxides, barium carbonate and a suitable binder; the lower end of the cardboard has a thicker coat of paste. The frame of the electrolyzer is made of asbestos cement board with perforated iron cathodes and diaphragms arranged on both sides; the profiles are chosen so that the anode compartment is as narrow as possible. The upper part of the electrolyzer consists of an asbestos-cement cover partially dipped into the anolyte. The electrodes pass through the cover which is provided with a chlorine outlet. Mild steel frames with openings for the hydrogen and caustic solution removal are attached to the cathodes and the whole apparatus has side walls made of mild steel plate. Fresh brine is fed into the asbestos cement frame by pipes. This electrolyzer has an advantage as it is easy to assemble, simple to operate and to control. The electrolyzer is besides that not oversensitive to shutdowns because the comparatively small volume of the anolyte is quickly heated to the required temperature when starting the operation again.

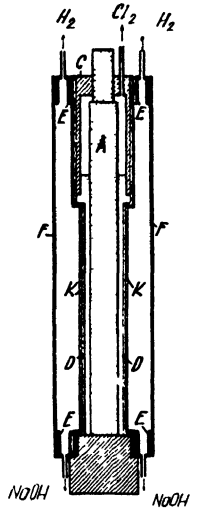


Fig. 92. De Nora's electrolyzer
A — Graphite anode, *K* — Perforated iron cathode, *C* — Asbestos-cement cover, *D* — Diaphragm, *E* — Iron frame, *F* — Iron plates.

According to available references this electrolyzer was designed for a load of 2000 A, the current density on the anode being about 8 A/sq. dm. The voltage across the electrolyzer was 2.8 to 3.5 V at 80 to 90 °C. Current efficiency was

around 90 per cent and the concentration of NaOH in caustic solution was between 100 and 120 grams per litre.

The anode compartment of the "*Krebs*" *electrolyzer* is formed by an independent, closed box which can be easily dismantled and taken out of the cathode compartment (see Figs. 93 and 94).

The upper supporting frame *W* of the electrolyzer is made of T-shaped irons to which a perforated sheet box *K* is welded in the form of two U's. The inside walls of the box are lined with several layers of asbestos paper with increased thickness from top to bottom in proportion to the increased hydrostatic pressure. Hydraulic seal *A* is now replaced by packing ring in more up-to-date units. The cover of the electrolyzer is made of slate in which gra-

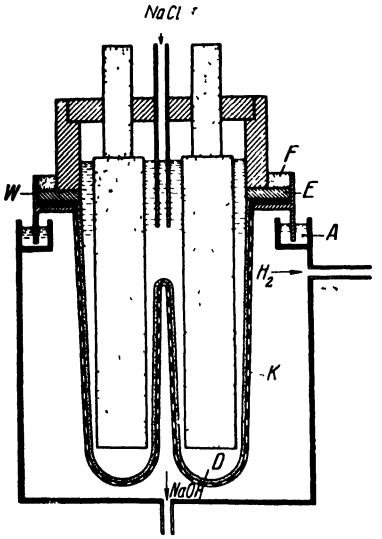


Fig. 93. "Krebs" type diaphragm electrolyzer

A — Water seal, *D* — Diaphragm, *F* — Insulating joint, *K* — Cathode of perforated MS sheet, *W* — Supporting frame.

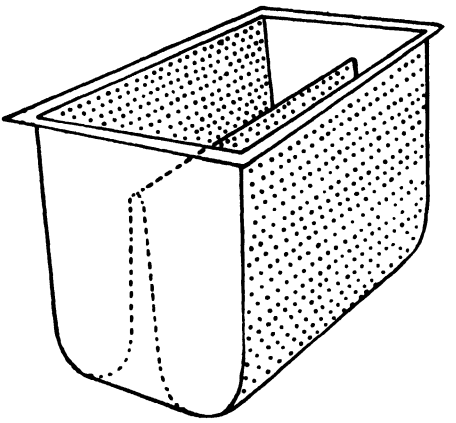


Fig. 94. Cathode of the "Krebs" electrolyzer

phite anodes are fastened through which chlorine is taken off. Fresh brine is fed into the cell through an automatic level controller. The remaining component parts can be clearly seen in the picture. The cell is loaded with 4000 A and its dimensions are $2300 \times 950 \times 520$ mm. It consists of two units closely fitted together. At a current density of 6 A/sq. dm on the surface of the diaphragm the temperature of the electrolyte is close to 70 °C. Current efficiency is about 93 per cent and the caustic solution produced contains about 120 grams of NaOH and 0.6 gram $NaClO_3$ per litre; the chlorine leaving the electrolyzer is 95 per cent pure and contains about 1.5 per cent of carbon dioxide.

The permeability of the asbestos diaphragm is considerable at the start of the operation but becomes normal after 5 to 6 days of "forming". The voltage applied equals 3.7 V with new electrodes; with graphite electrodes operating

a long time higher values are attained, up to 4.3 V, owing to their increased distance from the cathodes. During operation the brine level is slowly raised to prevent a decrease in the rate of percolation resulting from the pores becoming clogged.

Townsend has found another solution to the problem of nonuniform hydrostatic pressure of the anolyte acting upon the diaphragm; in his electrolyzer (Fig. 95) the cathode compartments are not empty but filled with mineral oil having 0.8—0.95 specific gravity. Here the difference in pressure acting on the upper and the lower part of the diaphragm is one third of the difference encountered in electrolyzers described up to now. Apart from this the backpressure of oil lowers the static pressure acting on the diaphragm, so that it can be made thinner (this permits to decrease the voltage at unchanged current or to increase the current at unchanged voltage).

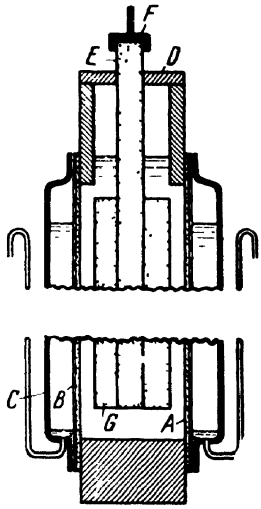


Fig. 95. Townsend electrolyzer

A — Diaphragm, *B* — Cathode, *C* — Side plates, *D* — Cover, *E* — Graphite conductor (lead in-to anode), *F* — Anode connection sleeve, *G* — Graphite anode.

This electrolyzer has a U-shaped concrete frame; on the open sides diaphragms *A* are fastened; these are made of asbestos cloth covered with a paste of iron oxide, asbestos powder and colloidal ferric oxide. Cathodes *B* made of perforated MS sheet are placed tightly against the diaphragms. Iron plates *C* form pocket-like compartments and serve as side walls. The diaphragms and the side plates are sealed with rubber inserts and clamped together. The internal walls of the iron side plates are given a protective coat of paint against corrosion by chlorine. The electrolyzer is closed by cover *D* through which the stems of graphite electrodes *E* pass; the stems are fitted with sleeves *F* which are connected to the source of current. The level of the brine must be the same as that of oil, or slightly higher, so that the brine can percolate through the diaphragm into the cathode compartments and sink to the bottom of the oil chamber into the collecting pockets, whereupon it may be drained off through the siphons Hydrogen bubbles through the oil layer and is taken off at the top of the cathode compartment.

At a voltage of 4.6 and 5.2 V a caustic solution is obtained which contains 125 to 140 grams of NaOH per a litre of solution; the current efficiency is some 94 per cent. The anode current density is fairly high, 10 to 15 A/sq. dm. The temperature of the electrolyte is about 60 °C.

Special care is to be taken to ensure that fresh brine is suitably fed to the electrolyzer; a satisfactory quantity of brine must be led in owing to the high current density used. Therefore, the brine is fed through several ducts on one side of

the concrete frame and taken off on the other side. The circulated brine is resaturated with common salt, chemically purified, filtered and returned to the electrolyzer.

The working cycle of these electrolyzers is about one month; the diaphragms must then be cleaned and a new layer of paste spread over them. After three months the damage caused to the diaphragms is so great that they must be renewed.

The chlorine leaving the anode compartments contains some 2 per cent carbon dioxide and 5 to 15 per cent air (the presence of air is due to a slight

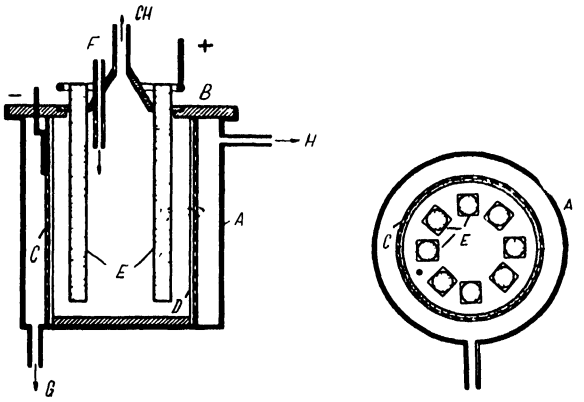


Fig. 96. The Gibbs-Vorce electrolyzer

A — Cylindrical vessel, *B* — Concrete cover, *C* — Cathode (perforated steel sheet or netting), *D* — Diaphragm, *E* — Anode, *F* — Brine inlet, *G* — Caustic solution outlet, *H* — Hydrogen outlet, *CH* — Chlorine outlet.

vacuum which is maintained inside the electrolyzer to prevent inconveniences arising through the escape of chlorine). These electrolyzers are designed for a load of 2500 to 5000 A.

One of the chief disadvantages of all electrolyzers with vertical diaphragms which have been described so far, is their comparatively complicated design which makes any repairs a lengthy affair. It has already been mentioned that vertical diaphragms become clogged with impurities much sooner than horizontal filtering diaphragms and require more frequent cleaning and replacement. Technicians, therefore, tried to design an electrolyzer in which assembly and dismantling should be as easy and quick as possible.

The *Gibbs-Vorce* electrolyzer is one of these; it is extremely simple and compact, so that for a current of 1000 A only some 1.4 sq. m of floor space is needed (in comparison with the horizontal Billiter electrolyzer which requires some 6.5 sq. m of floor space for every 1000 A).

The Gibbs-Vorce electrolyzer (Fig. 96) is a steel cylinder 660 mm in diameter

and 910 mm high. Inside the cylinder is a cylindrical cathode of perforated steel sheet with a concrete bottom. The electrolyzer has a concrete cover which supports 24 graphite anodes (cross section 51 × 51 mm, length 920 mm), arranged at equal distances apart in a circular way. The lid is provided with a glass tube for the chlorine outlet and an opening for the brine inlet which is automatically controlled by a level float and a level gauge. The caustic solution is withdrawn through an opening in the bottom of the cathode compartment.

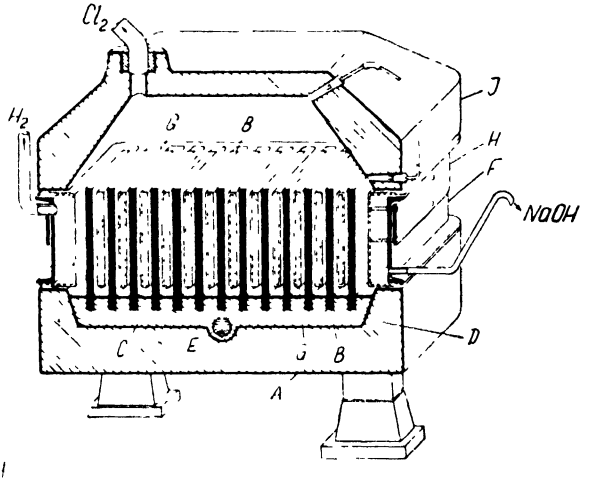


Fig. 97a. The Hooker electrolyzer (schematic drawing).

A — Concrete bottom of electrolyzer, *B* — Graphite anodes, *C* — Layer of lead in which the anodes are embedded, *D* — Protecting layer over the lead (made of cement and pitch), *E* — Copper conductor to anodes (embedded in the lead, *F* — Steel frame to which cathodes are welded, *G* — Hollow pocket cathodes (of steel netting), *H* — Copper conductor to cathode, *J* — Concrete top of electrolyzer.

Current is led to the cathode by a cable the other end of which is connected to the anode sleeves of the adjacent electrolyzer in series.

The inside of the cathode is lined with asbestos paper 0.6 mm thick. To achieve uniform permeability for brine three layers of paper are used in the lower part of the electrode and only two in the upper part.

Electrolyzers which are connected in series including those of 68 to 70 units are placed on insulators which rest upon concrete stands. An overhead travelling crane transports the electrolyzers to the workshop if the diaphragms or anodes have to be replaced or for any other repairs.

The first Vorce electrolyzer was built for a load of 1000 A; electrolysis was performed at 7 A/sq. dm, 75 °C, and some 3.8 V. Current efficiency was 91—95 per cent and one litre of solution produced contained about 100 grams of NaOH, 190 grams of NaCl and 0.8 grams of $NaClO_3$. The chlorine was 95—96 per cent pure and contained between 0.8 and 1.5 per cent of carbon dioxide.

The recent model of the Vorce cell has been improved in such a way that an additional cylindrical cathode and diaphragm was placed into the middle of the anode space, so that also the inner surface of the anode was utilized for electrolysis. With this adaptation the electrolyzer can work with nearly twice the load of that of an electrolyzer with one cathode without any increase in dimensions.

Electrolyzers of this type utilize only about 60 per cent of the energy consumed; the rest of the energy is lost in the form of heat partly carried away by the products of the electrolysis, partly radiated into surroundings.

Hooker designed a new type of electrolyzer (see Fig. 97a, b) in which he succeeded in increasing the energy efficiency to 66 per cent; this was achieved by lowering the ohmic resistance of the bath almost to half its value by using a larger surface of the diaphragm and of the electrodes; moreover, the heat contained in the product of electrolysis was utilized to preheat the fresh brine fed into the electrolyzer. Apart from this, the designer used for his cell a nearly cubical shape which minimizes radiation losses and permits the cell to be operated at a higher temperature

This electrolyzer consists of concrete bottom A, cathode assembly F and concrete cover J. The concrete bottom A is shaped like a rectangular trough traversed by copper or mild steel bar E embedded into lead layer C; this bar is connected to the positive pole of the source of current. The lead is protected against the corrosive effect of the acid anolyte by a layer D of cement and pitch. The lower ends of 30 graphite anodes B, arranged in parallel rows, are embedded in the same conductive layer of lead. Each row of anodes consists of three plates the dimensions of which are 680 × 240 × 30 millimetres The concrete bottom supports the cathode assembly, made as a rectangular frame F on the opposite sides of which are welded hollow and flat cathode pockets G of corrugated steel gauze, projecting inwards. The cathode pockets are so arranged that when the electrolyzer is assembled they fit into the free spaces between the anodes. The cathode frame carries the cathode connection and is closed by cover J and the whole is clamped together by bolts.

In order to lower the solubility of the chlorine and to increase the conductivity of the electrolyte the brine is preheated by hot caustic solution which is leaving the tank. This is done by two concentric coils insulated on the outside which are inserted into the cathode frame. The caustic solution leaving the cathode pockets flows first through the coil and preheats the incoming fresh brine which is flowing in the opposite direction through the outside annular space before entering the electrolyzer. The temperature to which the brine is preheated is controlled according to the current flowing through the electrolyzer. This is carried out by putting out of operation a part of the heat exchanger coils. Both the level and the temperature of the brine are steadily checked with a level gauge and a thermometer.

Chlorine is taken off from the upper space under the concrete cover while hydrogen is drawn off through a side opening in the cathode frame.

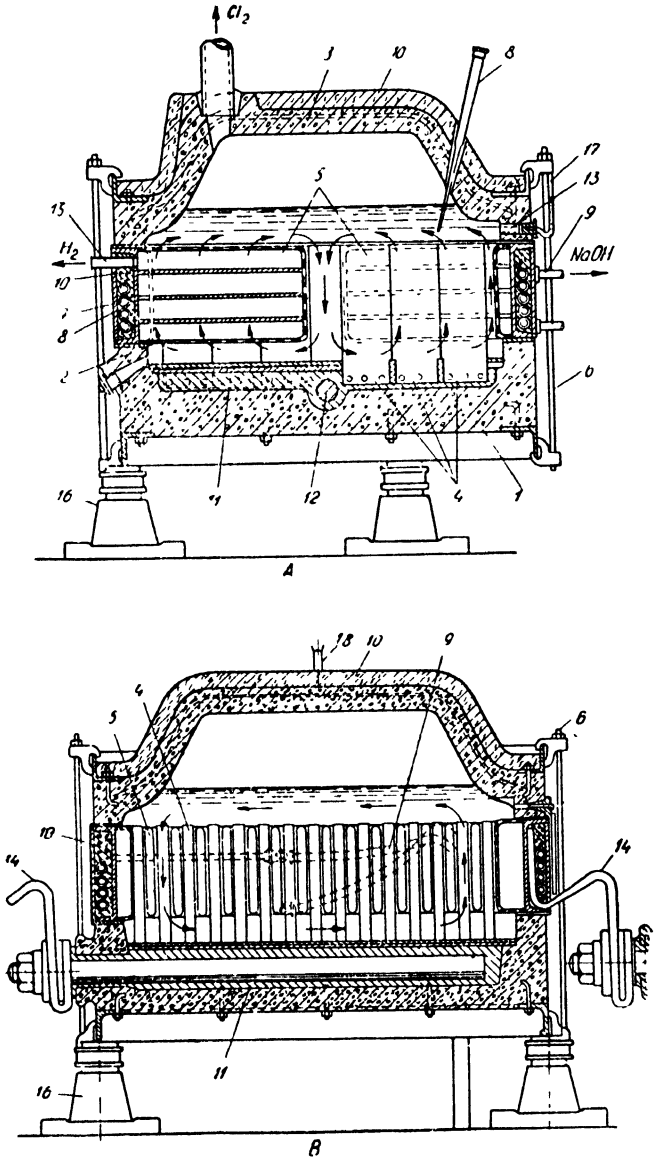


Fig. 97b. The Hooker type electrolyzer.

1 — Concrete bottom, *2* — Cathode frame, *3* — Cover, *4* — Graphite anodes, *5* — Cathodes made of corrugated steel gauze, *6* — Bolts, *7* — Coil for heating brine, *8* — Coil for cooling caustic solution, *9* — Caustic solution outlet pipe, *10* — Insulation, *11* — Lead layer, *12* — Main conductor to anodes, *13* — Feed of preheated brine, *14* — Main conductor to cathodes, *15* — Hydrogen outlet, *16* — Insulators, *17* — Brine level gauge, *18* — Thermometer.

The cathodes are enveloped on the outer side by an asbestos diaphragm which is formed by dipping the cathode assembly into a suspension of asbestos fibres in salt solution; then a suction is applied at the hydrogen outlet or caustic solution drain. During this evacuation the cathodes become coated with a sufficiently thick layer of asbestos. After some minutes the cathode is removed from the suspension and air is drawn through until the asbestos becomes dry and compact. It takes about one hour to make a new diaphragm.

The Hooker electrolyzer is manufactured in different sizes; the operating data are contained in the following table:

Current per electrolyzer	5000	6000	7000	A
Current density on the diaphragm	415	500	580	A/sq. m
Temperature of electrolyte	85	90	92	°C
Voltage across electrolyzer	3.28	3.35	3.45	V
Concentration of sodium hydroxide in caustic solution	135	135	135	grams per litre
Current efficiency	94	95	95.50	per cent
Energy efficiency	66	65	64	per cent
Service life of diaphragm	8	7	5	months
Service life of anodes	20	15	12	months
Floor space required per 1000 A	1.25	1.25	1.07	sq. m

The voltage across an electrolyzer built for a current of 10 000 A equals about 3.75 V while the floor space required per 1000 A equals some 0.75 sq. m only.

From the point of view of floor space required and with regard to energy yields the Hooker electrolyzer is more advantageous than any type of diaphragm electrolyzer described so far; it is in this respect even better than the modern mercury cathode electrolyzers. The best proof of the popularity and efficiency of this electrolyzer lies in the fact that its capacity has been gradually increased. Today units are built to work with currents as high as 20 000 and 30 000 amperes (types S-3 and S-3A).

b) *Production of chlorine and caustic solution in mercury cathode electrolyzers*

Modern electrolyzers of the diaphragm type yield caustic solution which contains up to 135 grams of sodium hydroxide per one litre of solution and sodium chloride between 180 and 130 grams. Such a solution is boiled down in evaporators to increase the concentration of caustic and to separate the remaining salt in solid form. A caustic solution evaporated to 50 per cent (i. e. containing 770 grams of sodium hydroxide per one litre) will still contain after the solid salt is separated 2 to 3 per cent of sodium chloride (as related to 100 per cent NaOH); although the amount of this admixture is comparatively small it can prove harmful in some applications (mainly in the manufacture of viscose).

With mercury cathode electrolyzers it is possible to prepare by a direct methode caustic solutions with a concentration of 50 per cent and more; a chemically pure product can be obtained if distilled water is used for the amal-

gam decomposition. This method, however, requires more electrical energy per unit weight of the product, higher first costs, and further a great amount of mercury to start the operation. Mercury cathode electrolyzers are more sensitive in operation so there must be more careful supervision in comparison with the diaphragm type electrolyzers. The ratio of production costs of the diaphragm and amalgam methods depends in the first place upon the price of the current and steam. The preparation of one ton of caustic solution containing 50 per cent of NaOH by the diaphragm method requires approximately 3000 kw.-hr. of alternating current for electrolysis and the driving of auxiliary machines as well as some 4 metric tons of steam for evaporation of the caustic solution (moreover 60 kw.-hr. of alternating current and 110 cubic meters of water). The energy needed for the amalgam method is equal about 3800 kw.-hr.; the corresponding losses of mercury amount to some 0.3 kg.

α) Theoretical principles

During electrolysis of alkali chloride only hydrogen will be liberated at an iron cathode, as its deposition potential is less negative than that of sodium or potassium. If, however, mercury is used as a cathode the situation is entirely different. Owing to the appreciable overvoltage of hydrogen on mercury and to the depolarization effect of this metal upon the deposition of alkali metal, diluted amalgam is formed (under given operating conditions) which is a solution of the compound $NaHg_4$ in mercury. The mutual relation of both potentials then changes. The deposition potential of hydrogen will become more negative and that of the alkali metal more positive till both potentials meet or the potential of the alkali metal even becomes less negative than that of hydrogen. So conditions exist for a simultaneous discharge of both alkali metal and hydrogen ions or even for nearly exclusive discharge of the ions of alkali metal.

For example, during electrolysis of sodium chloride (with unit activity of sodium ions) the reversible deposition potential of sodium $\pi^{\circ}_{Na^+/Na} = -2.714$ V; during deposition on circulating mercury, in which the concentration of sodium i skept at a constant value of 0.2 per cent, this potential equals —1.867 V.

The reversible potential of hydrogen in a neutral solution, $\pi_{H^+/H_2, Pt}$, equals —0.415 V. If, however, a mercury cathode is used, the first hydrogen bubbles only appear at a cathode potential of about — 1.26 V. At high current densities used in electrochemical processes mercury has a still greater overvoltage so that the deposition potential of hydrogen becomes still more negative. This negativity increases still further as the solution in the vicinity of the cathode becomes slightly alkaline soon after starting the electrolysis because a small amount of sodium dissolves in the electrolyte. In these circumstances hydrogen can only be liberated in noticeable quantity at a potential of a little above — 2 Volts. This potential is, however, more negative than the deposition potential of sodium on the surface of the amalgam so that under these operating conditions no noticeable quantity of hydrogen is actually liberated.

Therefore, the main processes occurring during the electrolysis of sodium chloride in an electrolyzer with a mercury cathode are represented by the following equations:

cathode: $Na^+ + e = Na$, (XI-25)

$Na + nHg = NaHg_n$,

anode: $Cl^- = 1/2\ Cl_2 + e$. (XI-26)

It has been already mentioned that the discharge of alkali metal ions at the mercury cathode is facilitated by the formation of amalgam which is a solution of compounds of alkali metal and mercury in mercury. This depolarization is more effective the more diluted the amalgam produced. If the concentration of amalgam is allowed to rise very high the deposition potential of the alkali metal assumes a more negative value which then approaches the deposition potential of hydrogen. At a higher concentration of amalgam a simultaneous evolution of hydrogen occurs, which is also facilitated by the fact that hydrogen overvoltage is less on more concentrated amalgam than on pure mercury. Finally, if the concentration of amalgam is such that it becomes viscous or solid depolarization no longer takes place and only hydrogen is evolved.

The alkali metal is deposited at the electrode surface and diffuses at a certain velocity into the interior of mercury. The course of the electrochemical process merely depends upon the composition of the phases at the boundary between the electrolyte and the electrode. The quicker the diffusion of the alkali metal from the surface of the mercury to the interior, the less risk there is of too concentrated amalgam being formed at the surface of the cathode and, therefore, less probability of hydrogen deposition.

For this reason rather diluted amalgams are used in technical practice with a content of alkali metals not exceeding 0.15 to 0.20 per cent. In order to promote diffusion of the alkali metal, mercury is allowed to flow slowly through the electrolyzer and the rate of flow is adjusted to the current applied in such a way that on leaving the cell the amalgam has a specified content of alkali metal. The amalgam is then led to a special decomposition trough (the so called denuder section) where it is decomposed by water to give hydroxide solution and hydrogen. The "denuded" (liberated) mercury together with the remaining small content of sodium or potassium (not exceeding 0.02 per cent) is returned to the electrolyzer. The circulation of mercury prevents any local oversaturation of the amalgam and ensures the necessary conditions required for the exclusive discharge of alkali metal ions.

The deposition of hydrogen is also prevented by maintaining a high concentration of salt in the electrolyte; this facilitates the discharge of alkali metal ions at a lower, i. e. less negative potential. For this reason saturated brine is fed into the electrolyzer and its rate of flow is so adjusted that on leaving the electrolyzer it still has a sufficiently high concentration; the depleted brine is then purified, resaturated with solid salt and returned to the process.

The cathode process is also influenced by current density because hydrogen overvoltage decreases with decreased current density which results in greater liberation of hydrogen; for this reason the load on the electrolyzer should not be allowed to drop below a certain minimum value.

Some current losses at the anode are caused by two reactions of chlorine which is partially soluble in the brine. The first is due to the diffusion of dissolved chlorine toward the cathode where a retrogressive reduction occurs according to the equation:

$$Cl_2 + 2e = 2\ Cl^- \quad . \qquad \text{(XI-27)}$$

The amount of cathodically reduced chlorine depends on the distance between the electrodes and rate of flow of the brine through the electrolyzer (i. e. on the intensity of stirring of the electrolyte).

The second reaction is due to hydrolysis of the dissolved chlorine which proceeds according to equations (XI-12) and (XI-13) under formation of hypochlorous acid and hypochlorite ions. As has already been stated hypochlorite ions are not stable products of electrolysis because they are easily oxidized at the anode to chlorate ions under the simultaneous evolution of oxygen [see equation (XI-14)]; this occurs even at a relatively low concentration of hypochlorite ions.

Analogously as with diaphragm cells a high concentration of brine and an elevated temperature have also here a favourable effect. Both factors reduce the solubility of chlorine in the brine and so suppress to a certain degree undesirable reactions (XI-12) — (XI-14). Higher temperatures have also an advantage as they lower the specific resistance of the electrolyte and accelerate the decomposition of the amalgam in the decomposition trough. On the other hand an excessive temperature lowers the hydrogen overvoltage on mercury whereupon the evolution of hydrogen on the cathode increases, the alkalising of the electrolyte is higher and more hypochlorite and chlorate are formed. High temperatures also shorten the service life of graphite electrodes as they become less resistant against the effect of anodically evolved oxygen. Taking into account these disadvantages with too high temperature as well as the limited durability of the rubber lining of the cells it is thought that the brine should leave the electrolyzer at a temperature of 75 to 80 °C.

Current efficiency

The secondary reactions mentioned occur to a comparatively small extent when platinum anodes are used; then current efficiency is between 96 and 97 per cent and the amount of hydrogen contained in the chlorine is small (0.1 to 0.2 per cent).

With graphite anodes current efficiency is somewhat lower, mainly because oxygen overvoltage is lower, so that hydroxyl ions formed by the dissociation of water may also be discharged apart from chloride ions. Evolution of oxygen is also caused by the porosity of the graphite because the chloride content in

the electrolyte in the cavities will be quickly depleted and then water will be decomposed under evolution of oxygen. Due to the discharge of hydroxyl ions hydrogen ions are set free and the acidity of the medium surrounding the anode increases. Hydrogen ions so formed migrate or diffuse to the cathode and decrease the deposition potential of hydrogen. Under these conditions more hydrogen is liberated at a mercury cathode than at a platinum one.

Another reason for the somewhat higher current loss with graphite electrodes is the crumbling of small particles of carbon which contaminate the surface of the mercury. As graphite displays a much lower hydrogen overvoltage than mercury there is a marked evolution of hydrogen on the contaminated spots. The particles of graphite in contact with mercury also decompose the amalgam already produced under liberation of hydrogen and formation of hydroxyl ions which in turn support an increased deposition of oxygen at the anode.

It is therefore clear that the quantity of hydrogen contained in the chlorine will be greater when using graphite anodes (about 1 per cent) than with platinum electrode. If electrolysis does not proceed well or if attendance is not careful enough the amount of hydrogen contained in the chlorine can attain five per cent or more which will cause an explosion in the electrolyzer.

The secondary reactions already discussed which take place when graphite anodes are used lower the current efficiency to 93—95 per cent. In spite of this lower current efficiency graphite anodes are preferred in practice because of the much lower first costs, compared with platinum electrodes.

The hydrogen content in chlorine is unfavourably influenced by the presence of calcium and magnesium ions in the brine. If these ions have a higher concentration they are discharged at the cathode and give unstable amalgams which are easily decomposed by water. The resultant insoluble calcium and magnesium hydroxides form sediments which contaminate a great part of the mercury surface, so that only a small area is left for the sodium or potassium ions to be discharged on. Under such conditions the amalgam easily becomes oversaturated and a great quantity of hydrogen ions start to discharge together with ions of the alkali metal.

Magnesium is particularly believed to cause increased evolution of hydrogen; it must be, therefore, very carefully removed.

Vanadium contained in some kinds of graphite has also a detrimental influence. Even a negligible trace of this element in the electrolyte can greatly impair the normal operation. The same pernicious influence also show chromium, molybdenum and nickel.

When the brine is purified sulphate ions are also removed as they increase the anodic evolution of oxygen by which graphite losses are raised.

A low hydrogen overvoltage is also encountered on iron. For this reason iron must never come into direct contact with the electrolyte. When rubber-lined electrolyzers are used the quality of the rubber and reliable application of the lining is of the utmost importance. Iron in the brine is also highly undesirable and therefore, it must be removed as carefully as magnesium.

Decomposition voltage

The theoretical decomposition voltage of sodium chloride may be calculated as the sum of the reversible oxidation potential of the chlorine electrode and the reversible reduction potential of the amalgam electrode.

$$E'_{min} = \varepsilon^{\circ}_{Pt,Cl_2|Cl^-} + \pi_{Na^+|NaHg} = -1.358 + (-1.867) = -3.225 \text{ V} \quad \text{(XI-28)}$$

$$E_1 = -E'_{min} = +3.225 \text{ V}. \quad \text{(XI-28a)}$$

The computed value E_1 indicates the theoretical decomposition voltage of sodium chloride in a solution with unit activity of both sodium and chloride ions if a reversible insoluble anode and a reversible amalgam cathode which contains 0.206 per cent of Na are used (at a temperature of 25 °C).

When comparing the theoretical decomposition voltage of sodium chloride on a mercury cathode and on an iron cathode [see equation (XI-18a) in the preceding chapter] it will be noted that this voltage has a value by about 1 V higher with a mercury cathode electrolyzer.

The operating voltage across an electrolyzer working at a given current load is still higher due to polarization voltage, i. e. mainly the chlorine overvoltage on the graphite anode and the value of voltage losses in the electrolyte and current conductors. In the case of a cell loaded by 15 A/sq. dm. at 65 °C the following distribution of the voltage was ascertained when electrolyzing brine with 25.5 per cent NaCl to obtain amalgam containing 0.2 per cent of sodium:

Cathode potential	1.738 V
Anode potential	1.334 V
Cathodic polarization	0.020 V
Chlorine overvoltage at the anode	0.300 V
Voltage loss in electrolyte	0.400 V
Voltage loss in current conductors	0.250 V
Total	4.040 V

Energy consumption

Because of a higher theoretical decomposition voltage mercury cathode electrolyzers have also a higher theoretical energy consumption. If for the preparation of 100 kg of sodium hydroxide 67 kA-hr. are required according to Faraday's law, then the theoretical energy consumption equals

$$W_t = 3.225 \cdot 67 = 216 \text{ kw-hr.}, \quad \text{(XI-29)}$$

instead of 146.5 kw-hr. required for the operation in an electrolyzer with iron cathode.

The actual consumption of energy can be calculated from the operating voltage across the cell and the current efficiency according to the equation (XI-20) which has been referred to when electrolyzers with iron cathodes were discussed.

The difference between theoretical and actual energy consumption is lower with mercury cathode electrolyzers than with diaphragm or bell-jar electrolyzers as there are less secondary voltage losses (there is no diaphragm and the distance between electrodes is three to four times shorter).

Decomposition of amalgam

It has been mentioned that amalgam is taken off from the electrolyzer after being enriched by some 0.2 per cent Na; it is led into a decomposition vessel shaped like a tower or a trough and here decomposed by water according to equation:

$$NaHg_n + H_2O = NaOH + \\ + 1/2\ H_2 + n\text{Hg}. \quad \text{(XI-30)}$$

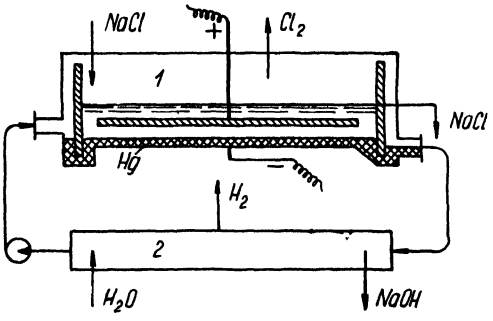


Fig. 98. Schematic drawing of a mercury cathode electrolyzer
1 — Electrolyzer, *2* — Trough for amalgam decomposition.

Liberated mercury containing not more than 0.02 per cent of Na is continuously returned to the process.

Fig. 98. illustrates this operation.

A thin layer of mercury is allowed to flow slowly on the bottom of electrolyzer *1*, then it enters decomposition trough *2* where water is continually supplied; the hydrogen and the caustic solution are drawn off from the decomposition trough as the final product while "denuded" mercury is returned to the process. At the same time saturated brine is fed into the electrolyzer; it flows on the surface of mercury and is led out at the other end of the electrolyzer slightly depleted of sodium chloride; it is then purified, resaturated and recirculated. Chlorine liberated at the anode is drawn off from the space below the cover of the electrolyzer.

The decomposition of alkali metal amalgams by water proceeds very slowly owing to the high hydrogen overvoltage on mercury. The rate of this chemical decomposition increases with temperature which reduces the hydrogen overvoltage, but this is still insufficient for technical practice.

The rate of decomposition can be considerable increased by allowing the hydrogen to evolve without overvoltage at a suitable material (such as iron or graphite, the latter is more suitable) which dips into the amalgam and caustic solution at the same time. Such a system acts like a galvanic cell with the amalgam as the negative electrode, at which sodium or potassium enter the solution, and iron or graphite as the positive electrode where the hydrogen is allowed to evolve. The theoretical value of the electromotive force of this cell

can be calculated as the sum of the equilibrium oxidation potential of the amalgam electrode and the reversible reduction potential of the hydrogen electrode:

$$2\ NaHg_n = 2\ Na^+ + n Hg + 2e;\ \varepsilon_{NaHg\,|\,Na^+} = +\ 1.867\ V; \quad \text{(XI-31)}$$

$$2\ H_2O + 2e = H_2 + 2\ OH^-;\ \pi_{OH^-\,|\,H_2,\,Pt} = -\ 0.828\ V; \quad \text{(XI-32)}$$

$$2\ NaHg_n + 2\ H_2O = 2\ Na^+ + 2\ OH^- + H_2 + n Hg;\ E_2 = 1.039\ V. \quad \text{(XI-33)}$$

It will be seen that the electromotive force E_2 of the reversible galvanic cell which consists of an amalgam electrode (0.206 per cent Na) and of a hydrogen electrode in a solution of sodium hydroxide of unit mean activity equal 1.039 V.

As the amalgam electrode is connected by a conductor to the electrode at which the hydrogen is liberated (Fe or graphite extends into both amalgam and electrolyte), the current passing through the cell is

$$I = \frac{E_2 - E_p}{R + r}, \quad \text{(XI-34)}$$

where E_2 stands for *EMF* of the cell, *Ep* for polarization of the electrodes, R is external resistance and r internal resistance which depends upon the electrical conductivity of the electrolyte and the distance between the electrodes. The analysis of this equation gives immediately the conditions promoting the rate of decomposition of the amalgam which is proportional to the discharge current I of the considered galvanic cell. It will be seen from this equation that the value of I at a given *EMF* will be greater the lower the value of polarization and of internal and external resistance.

The polarization is caused by concentration polarization and overvoltage at which hydrogen is evolved at the electrode. Concentration polarization can be lowered by stirring the amalgam. This is done by allowing the amalgam to flow through the decomposition trough at a suitable rate.

Overvoltage can be lowered if suitable material is used for the positive electrode and if it has a large surface area enabling current density to be lowered. Today, graphite is exclusively used for this purpose; it is formed as a so called grid the surface of which is made as large as possible by suitably shaped ribs.*) Iron grids were previously used but after some time they became coated with amalgam, and so have lost their activity.

The external resistance R which consists of the resistance of amalgam, graphite and contact resistance between them is of minimum value in this arrangement, because amalgam comes into direct contact with the graphite grid.

When unsoftened water is used for decomposition, calcium and magnesium

*) The surface of the graphite ribs is sometimes preactivated by being dipped into a solution of ferric chloride, then soaked in chlorine water and finally dried. Otherwise the grids can be steamed for three hours and then activated by being soaked with a copper sulphate solution.

salts contained in it are precipitated in the alkaline medium and the sediment formed may considerably increase the contact resistance. In order to overcome this obstacle, water is softened by means of cation exchangers (wofatites) to 0.5 degrees of hardness (German). The use of softened water allows to maintain the activity of the graphite for a long time.

For manufacturing chemically pure caustics distilled water is used for the decomposition of amalgam.

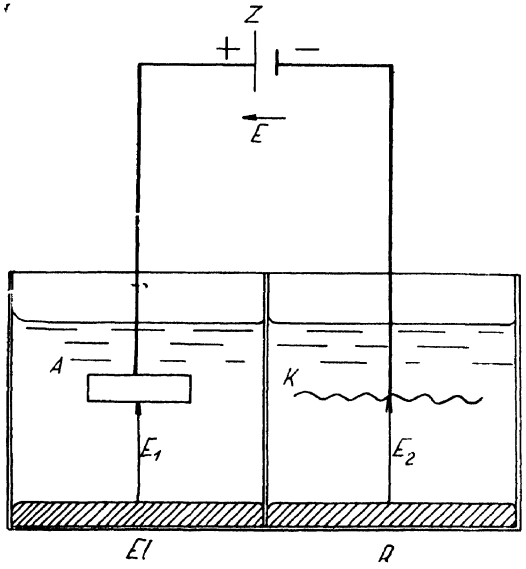


Fig. 99. Diagrammatic representation of electrolyzer and decomposition trough. Z — Current source, E_1 — Electrolyzer, R — Decomposition trough, A — Graphite anode, K — Graphite grid, E_1 — Sodium chloride decomposition voltage, E_2 — Amalgam cell voltage.

On decomposing the amalgam as described the liberated energy is wasted by being converted into heat. However, attempts have been made at utilizing the electromotive force of the amalgam cell for the decomposition of salt. According to projects made, both electrolyzer and decomposition trough should be connected to the source of current in the manner shown in Fig. 99. It is evident, that the mercury cathode electrolyzer E_1 is fed from the source of current Z and also from the decomposition trough R which are connected in series so that their EMF's are added. Assuming reversible operating conditions following equation is valid:

$$E + E_2 = E_1. \qquad \text{(XI-35)}$$

In this equation are $E_1 = 3.225$ V the theoretical decomposition voltage of

the sodium chloride in the electrolyzer, $E_2 = 1.039$ V the *EMF* of the amalgam cell in the decomposition trough and E the voltage of the current source.

After substituting these values we obtain $E = 3.225 - 1.034 = -2.186$ V. According to this the voltage of the current source necessary for the decomposition of salt in a mercury electrolyzer theoretically should be equal to that used for the production of alkali hydroxides in an electrolyzer with iron cathodes. Consequently, the mercury would only act as a vehicle transporting the sodium to the decomposition vessel, and the excess energy consumed for the formation of the amalgam would be regained during its decomposition. This system could operate in this manner only under reversible conditions, i. e. at an infinitesimal current because only in this instance the polarization on the electrodes and losses due to internal resistance are almost zero. During electrolysis a considerable current flows through the system and the voltage across the amalgam cell is lower due to the ohmic resistance of the electrolyte and polarization. The most detrimental is polarization which is mainly caused by a slow diffusion of the sodium from inside the amalgam to its surface. Because of this insufficient rate of diffusion the surface of the amalgam becomes soon depleted of sodium and the voltage E_2 across the amalgam cell drops to zero and later becomes even negative, i. e. the polarities of the cathode and the cathode change due to polarization phenomena. This means that the system $NaHg_n \mid NaOH \mid C$ would actually not operate as a galvanic cell but as an electrolyzer consuming some energy from the external source of current. For this reason the idea of reducing the voltage across a mercury cathode electrolyzer could only be exploited under conditions which are very improbable to be achieved: it would be necessary to spread the amalgam in form of an infinitely thin film over a very large surface, i. e. to shorten considerably the path of the sodium diffusing from the interior of the amalgam to its surface and limit the current density to a sufficiently low value.

β) Designs of Mercury Electrolyzers

The amalgam method of chlorine and caustics manufacture was simultaneously discovered by Castner and by Kellner, who unaware of each other applied independently for patents (1892). After an initial competitive fight the two research workers united their efforts and sold their patent rights to the firm of Solvay Co. Manufacture on industrial scale was started under the name of Castner-Kellner. Technical improvement of this method is chiefly the merit of I. G. Farben in Germany. Since 1925, the method has been used also by the Czechoslovak Society for Chemical and Metallurgical production at Ústí n. L. (formerly Aussig), where further improvements were made. A number of design modifications as well as the solving of various problems applying to important parts of equipment represent a valuable contribution of this company to the development of the mercury electrolyzer.

Since then the design of the electrolyzer was perfected and its capacity was gradually increased. At present, units built for 24.000 A or higher current loads

are quite common.*) According to the position of the electrodes, the electrolyzers are divided into horizontal and vertical types.

Horizontal electrolyzers

The description of a horizontal electrolyzer given below concerns a unit operating under a current load of approximately 20 000 A. The electrolyzer has a shape of an an iron trough 14.000 mm long and 600 mm wide. Parallel to the electrolyzer equally long and 300 mm wide decomposition trough (denuder) is located. The two sections are hydraulically connected, at one end by

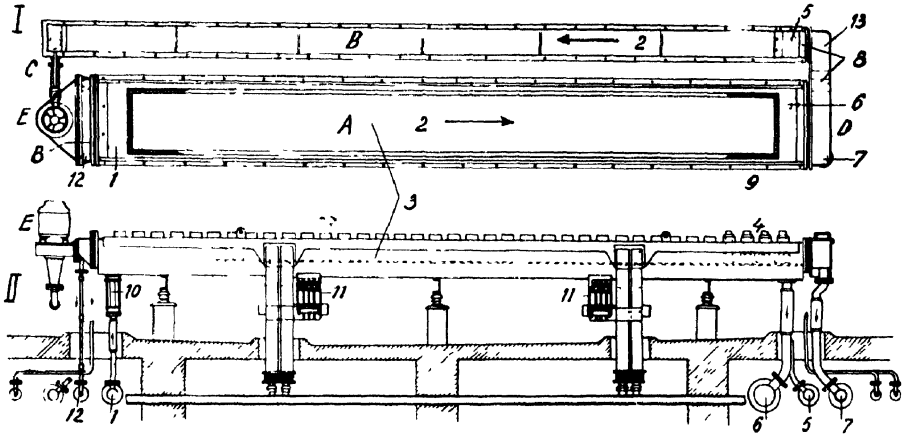


Fig. 100. Horizontal mercury electrolyzer.

I — Top view, *II* — Side view, *A* — Electrolyzer, *B* — Decomposition trough (denuder), *C* — Front connecting device, *D* — Rear connecting device, *E* — Mercury circulation pump, *1* — Brine inlet, *2* — Flow direction of mercury and brine, *3* — Iron cathode, *4* — Graphite anodes, *5* — Caustic solution and hydrogen outlet, *6* — Depleted brine and chlorine outlet, *7* — Degasing, *8* — Partition plates, *9* — Rubber lining, *10* — Rotameter, *11* — Switch, *12* — Water inlet, *13* — Purifying chamber.

the front connecting device and an elbow pipe, at the other end by the rear connecting device, so that the amalgam is circulated from the electrolyzer into the denuder and from its end to the front of the electrolyzer.

Along the bottom of the electrolyzer (Fig. 100 and 101) the mercury flows which acts as a cathode. Fresh saturated brine is introduced into the electrolyzer and flows in the same direction as the mercury. When passing through the cell the mercury becomes enriched with sodium and at the same time chlorine is evolved at the anodes which are fastened to the cover of the electro-

*) According to latest informations, electrolyzers working under a current load of 48.000 A have been put into operation, whilst units for a 100.000 A current load are being designed.

lyzer. The brine which has lost a part of its sodium chloride content is drained away from the bottom of the electrolyzer, while the amalgam flows into the denuder through the rear connecting device.

In order to prevent the brine and the chlorine from penetrating into the denuder, partition plates (not reaching the bottom) which act as hydraulic seals are placed conveniently both in the rear and in the front connecting device. In the denuder, the amalgam is decomposed by water into caustic solution and hydrogen. Partition plates at both ends of the denuder prevent the caustic solution and the hydrogen from penetrating into the electrolyzer. The mercury which is almost free of sodium or potassium is pumped into the front connecting device, from where it returns to the electrolyzer. While the mercury is circulated through the whole system, i. e. from the electrolyzer into the rear connecting device and then into the denuder and finally through the frontal connecting device back to the electrolyzer, the caustic solution and hydrogen are confined to the denuder while the brine and chlorine remain within the electrolyzer.

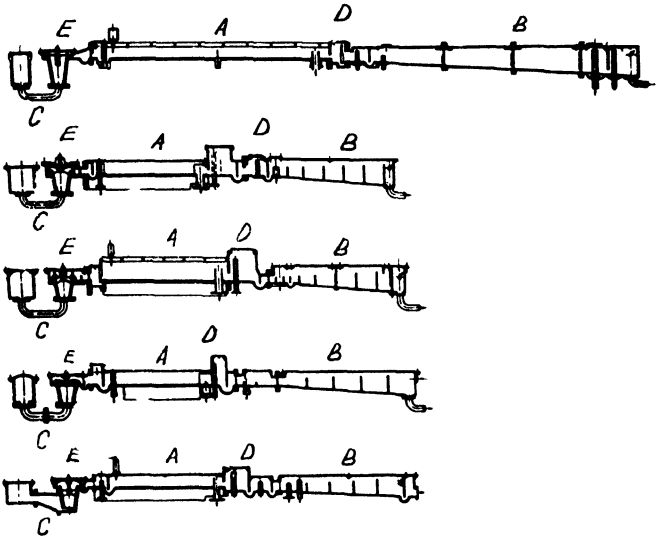


Fig. 101. Schematic representation of various types of horizontal mercury electrolyzers (side views):

A — Electrolyzer, *B* — Denuder, *C* — Front connecting device, *D* — Rear connecting device *E* — Mercury pump, *1* — Brine inlet, *2* — Outlet of depleted brine containing chlorine, *3* — Flow of mercury, *4* — Water inlet into front connecting device, *5* — Water inlet into denuder, *6* — Outlet of caustic solution and hydrogen, *7* — Partition plates, *8* — Covers, *9* — Graphite anodes, *10* — Graphite grid in denuder.

In the drawing, the denuder is shown in series with the electrolyzer, whilst in reality it is located parallel to it.

There are different designs of electrolyzer bodies. The body may consist of

an H-shaped beam, the central part of which forms the bottom of the electrolyzer and is machined (Fig. 102), or else the bottom is fabricated of a thick iron plate to which two U-shaped beams are bolted, and so form the walls of the electrolyzer (see Fig. 103).

The inner sides of the walls are coated with vulcanised natural rubber or P.V.C. In an electrolyzer of the described size the bottom measures 660 sq.dm and is not coated. It is electrically connected to the main cathode bus-bar, located on the insulators under the cell. Older models had walls and the bottom made of concrete and the current was led in by iron disks, inserted into

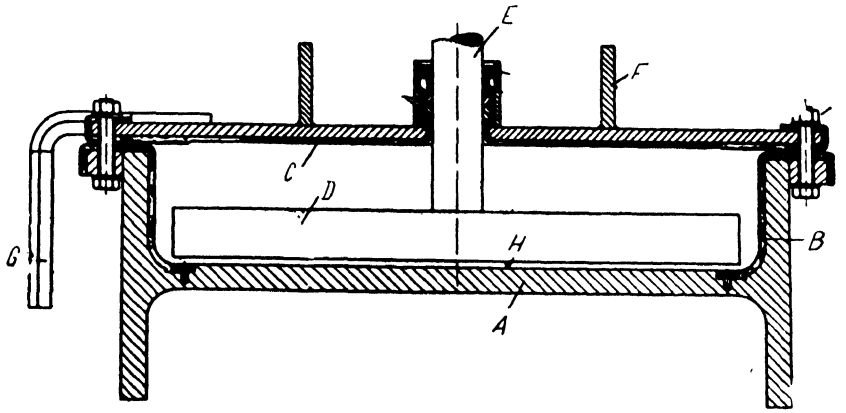


Fig. 102. Horizontal mercury electrolyzer.
A — H-shaped iron beam, *B* — Rubber-lined side walls, *C* - - Rubber-lined iron cover, *D* - - Graphite anode, *E* — Graphite stem, *F* — Reinforcing ribs, *G* — Bus-bar connection to anodes, *H* — Iron cathode.

the bottom. The bottom of the electrolyzer slopes slightly (4—8 mm to a 1000 mm length) to enable the mercury to flow at a speed of some 100 to 200 mm/sec. A layer of mercury some 2 to 4 mm thick covers the bottom of the electrolyzer. The electrolyzer is closed with a cover made of iron coated inside with rubber. The cover is sealed with rubber gaskets and bolted to the trough of the electrolyzer. The positive current is conducted from the main anode bus-bar into the cover, and then by flexible bands and sleeves to a row of 72 graphite stems which are impregnated with linseed oil. The bottoms of the stems are screwed into the graphite plate anodes (size 500 × 175 × 60 mm) which are provided with holes for chlorine escape. The spacing between the anodes and the surface of the mercury is 3 to 6 mm. The total surface area of the anodes amounts to 630 sq. dm. Saturated brine, at a temperature of 50 °C enters through a rubber-lined pipe from the distributing manifold in the electrolyzer either through the bottom or through the cover. The quantity of brine is registered by a rotameter and controlled by a throttle valve. The brine which

flows on top of the mercury in a layer 10 cm deep leaves the electrolyzer at 80 °C through a branch in the bottom of the trough, together with the chlorine, and is collected in a rubber-lined iron pipe. A separator for chlorine and brine is located under the electrolyzer and is connected with the collecting pipe for spent brine and chlorine. Other models do not provide for the chlorine to be discharged together with the spent brine; it is drawn off by a separate pipe from the space below the cover at the rear of the electrolyzer.

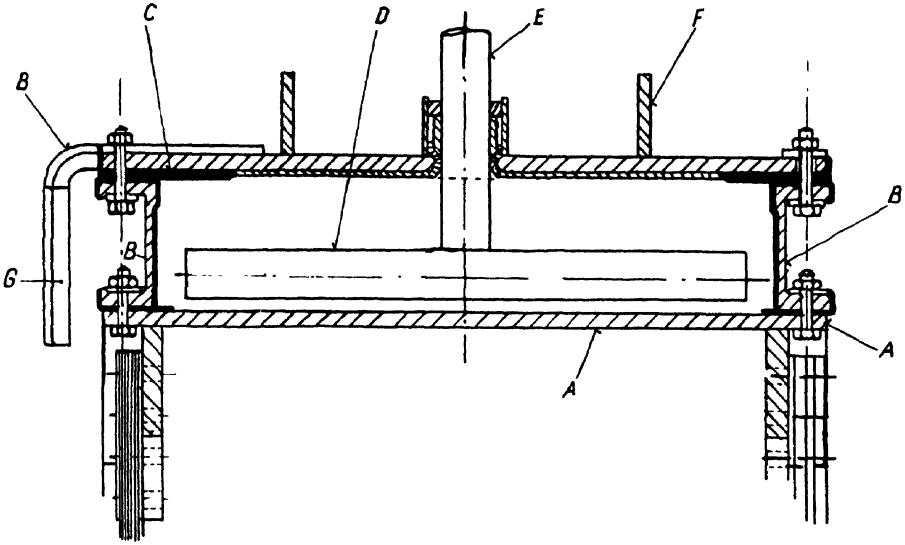


Fig. 103. Horizontal mercury electrolyzer (cross section):
A — Thick iron plate bottom, *B* — Rubber-lined side walls consisting of *U*-beams, *C* — Rubber-lined iron cover, *D* — Graphite anode, *E* — Graphite stem of the anode, *F* — Reinforcing ribs, *G* — Bus-bar connection to anodes.

The rear connection device is made of rubber-lined iron. It has a partition plate under which the amalgam flows into the denuder. Between the rear connecting device and the denuder two partition plates form a purification chamber with a rubber-plated iron lid.

The denuder is either rectangular in shape and made of welded iron plates or it is made of an iron pipe, 200 mm in diameter which is blinded at the ends. The inner walls may be rubber-lined. Rubber-lined denuders are used wherever the caustic solution must be free of iron. The same purpose is served if the denuder is made of cast iron which must not be lined with rubber.

The bottom of the denuder slopes in the opposite direction to the tilt of the electrolyzer (tilt approx. 8 mm to a 1.000 mm length) to allow the mercury which reaches the denuder from the rear connecting device to gravitate to the

other end of the trough. The mercury runs out at the low end of the trough through an elbow pipe into the collecting chamber from where it is lifted by means of the rotating cone of a vertical shaft centrifugal pump (connected to the front of the cast iron connecting device) to the highest liquid level in the electrolyzer. The mercury then passes under the seal plate and flows along the bottom of the electrolyzer. In the whole of the electrolyzer, including the denuder, some 800 to 900 kg of mercury are circulated.

If a breakdown in circulation occurs the mercury will leave the cell and the denuder and flow to the collecting chamber, denuding the iron bottom of the electrolyzer. Hydrogen then begins to be evolved. A float located in the collecting chamber causes a siren to sound. The number of the cell where the breakdown has occurred will flash on a signal panel. So the breakdown can be quickly repaired.

Softened water is supplied through a rotameter into the front connecting device between the partition plate and the mercury pump. It flows over the mercury level (washes the mercury) and enters the denuder through a pipe which is dipped under the level of the caustic solution. By this arrangement the escaping of hydrogen from the denuder is prevented. In the denuder water flows countercurrently to mercury and is withdrawn from the end of the denuder in form of a caustic solution.

Graphite grids or suitably shaped graphite plates are placed on the bottom of the denuder and are fixed by spacing bolts. There are grooves and holes in the graphite which give the grid the highest possible surface area. Amalgam together with a certain amount of caustic solution flows along the grids while liberated hydrogen escapes through the holes in the graphite and is drawn off together with the caustic solution through a pipe in the bottom of the denuder. Separation of hydrogen from the caustic solution together with the separation of small amounts of mercury entrained in the caustic solution is carried out in a system of two separators.

Some denuder designs have separate outlets for both hydrogen and caustic solution. Here the caustic solution is withdrawn through a rubber-lined pipe provided with a bell-type seal which prevents the hydrogen to escape together with the solution. The pipe passing through the bottom of the trough is connected with the main collecting pipe, by which the caustic solution is discharged through a mercury separator into the receiver. Above the caustic solution outlet there is a handling hole with a flange. It has a screwed-on lid. Apart from this there are two other handling holes in the trough, covered with lids. Through these the graphite grids are inserted and taken out. The hydrogen is drawn off by a special dome placed at the far end of the trough which is situated approximately above the caustic solution outlet.

At a current of 20.000 A and a total surface of the anodes amounting to 630 sq. dm, the current density at the anode equals 32 A per sq. dm. Such a relatively high current density can only be used if all the brine is perfectly purified prior to the operation and if the temperature upon entering the electro-

lyzer is maintained around 50 °C*). At this high current load maintained in the cell the voltage reaches approx. 4.5 V. The current efficiency amounts to about 95 per cent. The consumption of direct current per 100 kg of NaOH produced equals 320 kw.-hr. Chlorine is obtained 96 to 98 per cent pure, the remainder is composed of about 0.5 % hydrogen, 0.6 to 1.5 % carbon dioxide and 0.5 to 3 % air. When leaving the denuder trough, the hydrogen contains 99.5 to 99.8% H_2, 0.2 to 0.5% air and 60 to 80 mg of mercury in 1 cu. m.

For the production of 100 kg of a 100 per cent sodium hydroxide some 152 kg of NaCl, 0.5 kg of graphite and 0.03 kg of mercury are required in a properly operated plant. The caustic solution obtained in this way is much purer than that obtained from the diaphragm electrolyzers and its composition varies within the following limits:

Na OH	48 to 50 per cent
Na_2CO_3	0.1 to 0.5 per cent
Na Cl	0.0020 to 0.100 per cent
Na_2SO_4	0.0003 to 0.006 per cent
Al_2O_3	0.0005 to 0.003 per cent
Fe_2O_3	0.0001 to 0.001 per cent
Hg	0.01–0.1 mg per liter

The whole of the cell rests on four cast iron frames insulated from the floor by porcelain insulators. Between the insulators and the cell there are set screws by which the required tilt of the electrolyzer can be set and its position fixed. Brackets are fitted to frames to support the denuder trough. On the frames between the denuder and the electrolyzer small stands are placed which have small insulators carrying the copper or aluminium bus bars. Between the cathode and the anode bus bar is a current switch which is controlled from the floor. This is for switching the bath off the circuit during repair.

The water feed to the denuders is controlled by means of a distributing device placed above the cells. The water runs out of a horizontal rotating arm into a system of chambers, arranged in a circle. Each of the chambers has an outlet which leads into the denuder trough of individual cells.

Today electrolyzers are placed on the top floors of factory with the distributing and collecting piping under the ceiling. Connecting pipes leading to individual electrolyzers pass through rubber coated stoppers placed in the floor, to ensure insulation. Located in the cellar are tanks for the caustic solution, the spent brine as well as hydrogen and chlorine blowers and other auxiliary equipment.

Electrolyzers are electrically connected in series of up to 200 cells which are connected with a direct current supply station with a voltage of 900 V. With such a high voltage of direct current special attention must be paid to a perfect insulation of the whole equipment including piping. Defective insula-

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*) According to latest informations, some factories work already with a current density of 38 A per sq. dm. and sporadically even with a density of 48 A per sq. dm.

tion may cause not only a heavy loss of current but also severe injuries to the operators. For this reason as well as to prevent corrosion all iron pipings for brine and chlorine have a rubber lining. In order to improve insulation some establishments interrupt the flow of the brine to the individual electrolyzers as well as the flow of the discharged caustic solution by special bell-shaped flow interruptors, made of polyvinylchloride in which a continuous stream of a liquid is dispersed in droplets.

As a rule, chlorine is drawn off from the cell by a rubber coated iron ventilator, under a slight vacuum of 5 to 15 mm of water column, so as to prevent the chlorine escaping through any leak into the surrounding atmosphere. A higher degree of vacuum is undesirable and would cause the chlorine to be excessively diluted by air. In some rare instances the anode gas is drawn off under a slight overpressure, in order to obtain as pure a gas as possible. Careful servicing is necessary to avoid the works being infected by chlorine escaping through a leak in the electrolyzers. On the other hand, a slight overpressure of some 10 mm of the water column is maintained in the denuder, to ensure that air will not be sucked into the trough and to prevent forming of an explosive mixture.

The inlet of the softened water into the denuder is controlled so as to form a caustic solution containing some 50 per cent NaOH. A caustic solution containing up to 70% NaOH can be produced in a thermally insulated cylindrical denuder trough if the following conditions are fulfilled: the concentration of the amalgam is increased to 0.3% Na; the grids used are carefully activated; the amalgam enters the denuder with a temperature of 75—80 °C; the water flows concurrently with the mercury; the quantity of water is lowered. The temperature of caustic, on leaving the trough, reaches 105 to 110 °C.

During the operation the mercury pump must be kept in proper working order and the brine inlet correctly set, else with an insufficient inlet of brine hydrogen is set free in greater quantities in the electrolyzer and the consumption of graphite is increased. Further, measures must be taken to see that the brine is saturated and sufficiently pure, that the caustic solution is drained regularly and that the amalgam is decomposed to a sufficient degree, that all the contacts and sleeves at the anodes are in good order; also that fragments of graphite, dropping into the cell are carefully skimmed from mercury in the rear connecting device.

Results of the operation are checked chiefly by determining the hydrogen content in the chlorine. For this purpose a previously measured volume of anode gas is shaken with a solution of potassium hydroxide; from the volume contraction the amount of chlorine can be determined. To the balance of gas a measured volume of air will be added and the mixture will be driven through a heated capillary tube containing palladium wire. Hydrogen will be burned to water. Its volume will once more be determined from the volume contraction of the gas. A standard operation will yield about 0.5 per cent of hydrogen in chlorine, the upper limit is considered to be some 2 per cent.

Hydrogen must not contain more than 0.2 per cent oxygen. If this limit is exceeded the gas is let out into the atmosphere by a pipe leading above the roof of the works. The oxygen content is determined by an automatic recording analyzer or in the case of a breakdown of the latter, by means of a phosphorus burette, in which oxygen reacts with phosphorus and the volume of the oxygen is determined from the volume contraction of gas. Besides that a check should be kept of the concentration of both fresh and denuded brine, of the contents of alkali metal in the amalgam both prior and subsequent to decomposition, the concentration of the caustic solution, the temperature of the brine on the inlet and outlet, the voltage in each individual cell, etc.

Graphite anodes gradually wear, which causes the voltage across the electrolyzer to rise. For this reason, the spacing between the graphite electrodes and the level of the mercury must be set at regular intervals of some six weeks, so as to reduce the voltage to its original level. During this refitting the cell is switched off the electrical circuit and the pipework. The brine is drained away and the cell is uncovered. The anodes are removed from the covering plates which are placed on a wooden stand. After they have been cleaned and levelled they are set to a correct spacing from the bottom of the cell and fastened to the cover (i. e. they are grout with cement). The bottom of the cell is cleaned and repaired. The flow of the mercury is adjusted to the required speed, sleeves and contacts are cleaned and the cell is then refitted and put into operation. After a longer period also the grids are taken out of the denuder and the adhering salt removed by washing in hydrochloric acid. The grids are steamed and, if necessary, activated. An overhaul necessitates a complete dismantling of the electrolyzer. The rubber lining of the side walls must be repaired and all parts derusted, etc.

The total amount of mercury which the electrolyzer has been filled with averages some 850 kg of which approximately 4 per cent are lost in a year. This loss is caused by the oxidation of mercury to calomel by chlorine, the evaporation of mercury into hydrogen, and mostly by the mercury being let out during the cleaning and repair of the electrolyzers. In the course of operation certain impurities contained in the brine (Mg, Ca, Fe), in the construction material of the electrolyzer and the anodes (Cr, V) are retained in the mercury and form clots of butter-like consistency. This "mercury butter" is collected and the mercury regenerated either by washing with acids or by distilling in an iron retort under vacuum. The graphite mud which mechanically retains a certain amount of the mercury carried away during the electrolysis, is also collected in the rear connecting device and subjected to a similar treatment.

In the early stage of the development of mercury cells frequent explosions occurred since chlorine contained large amounts of hydrogen. At present explosions occur very rarely because their causes are known and generally the consequences are not fatal. The damage is usually slight i. e. the cover of the electrolyzer is loosened or the small inspection lids are flung off. The content of hydrogen in chlorine can increase for a number of reasons: if cold cells are

put into operation too suddenly, if the iron bottom is denuded as a result of a disturbance in the circulation of the mercury (especially in the pump), if the anode is broken off, if the alkali metal content in the recycled mercury is high or the content of impurities in the brine (Mg, Fe, Cr, V) is increased, or if the brine concentration is low and the brine flows through the electrolyzer too slowly, and also, if the graphite is of a low grade, yielding a lot of graphite mud. If a higher hydrogen content in chlorine is detected in time an explosion may be forestalled by eliminating the defect.

Vertical electrolyzers

Because of the relatively high floor space required by horizontal mercury, designers of electrolyzers turned their attention to the designs of vertical electrolyzers. The first was installed by the firm I. G. Farben in Germany.

The vertical electrolyzer (see Figs. 104 and 105) is an iron vessel, rubber-lined 2800 mm long, 2100 mm wide and 2200 mm high, divided into three compartments. The lower part has a semicylindrical bottom and is filled with mercury. It is connected to the negative pole of the current source.

A rotating shaft coupled with a rubber coated drum passes through the stuffing boxes in the walls of the quadrangular middle compartment. Five steel cathode disks are fixed on the shaft and are approx. 1800 mm in diameter. The rotor operates at 7 r. p. m. In order to reduce the dead volume of the idle mercury in the lower part, semicircular rubber-coated iron insertions are placed between the disks. The rest of the space is filled with mercury (total weight approx. 2000 kg) into which the lower parts of the rotary disks are dipped. The mercury inlet opens into the middle section. The mercury containing sodium amalgam leaves the middle section on the opposite side to be then transported into the decomposition vessel.

The upper section of the electrolyzer which is also rectangular in cross section, carries the graphite anodes, the hubs of which pass through the stuffing boxes in the walls of the container. The hubs are connected with the positive pole of the current source. The saturated and purified brine is brought through a rotameter from the manifold to the middle section of the electrolyzer, and almost fills it up to the overflow which is situated at the top of the container. Through the overflow, the depleted brine is discharged together with chlorine, which is then separated in a special separator and led into a chlorine collecting pipe.

The iron disks in contact with the mercury are amalgamated and whilst rotating they entrain a thin film of adhering mercury into the brine space between the graphite electrodes where electrolysis proceeds. At the anodes, chlorine is set free, whilst the alkali metal ions discharge at the mercury. Amalgam is formed and washed away when the disk passes through the mercury in the lower part of the electrolyzer. Amalgam is conducted to a mercury pump which drives it into a decomposition vessel (640 × 420 × 800 mm), sealed at

the top by a cover. The amalgam enters the vessel from above and passes first through a screen then through a layer of graphite ground to 2 to 3 cm lumps. Water is driven in the reverse direction and is drained off as caustic solution together with the hydrogen from the upper part of the tower immediately under the cover. The mercury freed from alkali metal is returned to the electrolyzer and enters on the side opposite to the amalgam outlet. This design of decomposition tower makes it possible to manufacture 70 per cent caustic solution without any difficulty as the temperature reaches 100 to 115 °C.

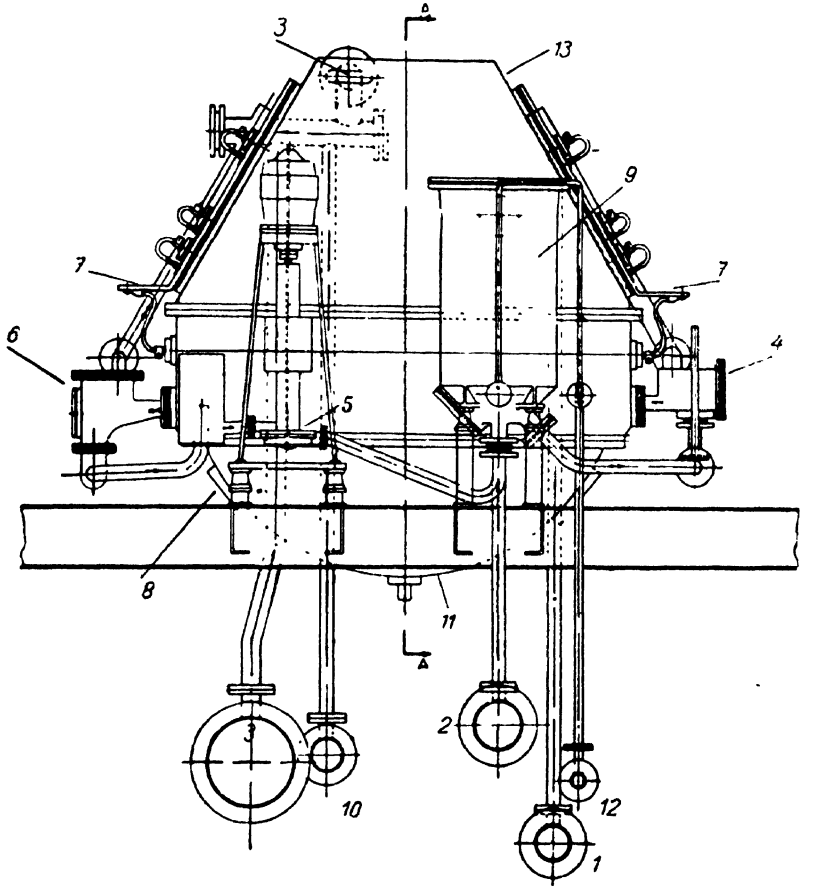


Fig. 104. Vertical rotary cathode mercury electrolyzer (side view).

1 — fresh brine inlet, *2* — NaOH solution and H_2 outlet, *3* — denuded brine and chlorine outlet pipe, *4* — mercury inlet, *5* — mercury pump, *6* — mercury outlet, *7* — current connection to anodes, *8* — current connection to cathodes, *9* — amalgam decomposition vessel filled with graphite, *10* — waste gas safety pipe (kept under vacuum), *11* — rubber lined iron vessel containing mercury, *12* — water pipe for decomposition vessel, *13* — electrolyzer lid.

These electrolyzers are designed for a load of 24 000 A With a spacing of 5 mm between the rotating disks and new graphite anodes the voltage across the cell amounts to about 4.3 V. With the gradual wear of the anodes the voltage increases up to 5.3 V, after which electrodes are replaced. Current efficiency reaches 91 per cent. The anode gas contains some 97 per cent chlorine and, as a rule, the hydrogen contains some 99.8 per cent H_2, the remainder being air.

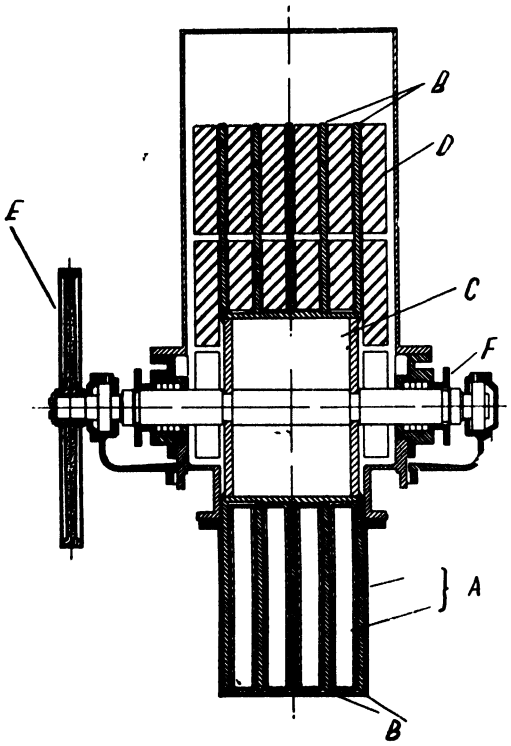


Fig. 105. Vertical rotary cathode mercury electrolyzer (section A--A from Fig. 104).
A — rubber-lined iron vessel with rubber-lined insertions, *B* — five rotary disks, *C* — rubber-lined drum, *D* — graphite anodes, *E* — pulley, *F* — shaft packing.

Rotary cathode electrolyzers take up a very little floor space not more than 0.2 sq. m. to each 1000 A. A disadvantage is that great mercury losses occur due to leakage in the bearings of the rotary cathodes and in the pump which transports the mercury into the decomposition vessel. The consumption of graphite is also abnormally high. Apart from this, current efficiency is lower and the content of hydrogen in the chlorine higher than with horizontal electrolyzers.

Another disadvantage of vertical decomposition towers is that the caustic solution contains a certain amount of fine graphite powder formed by abrasion of the graphite lumps. The hydroxide solution also contains a considerable quantity of mercury (approx. 5 mg per litre). In order to remove these impurities from the solution it is passed through candle filters made of sintered nickel powder and carbon.

The Mathieson Alkali Works in Arvida have developed a combination of a horizontal electrolyzer with a vertical amalgam decomposition tower into which the amalgam is driven by means of a centrifugal pump. The chief advantage of this type is a 40 per cent saving of floor space, compared with a standard horizontal electrolyzer. A special design of the anode sleeves was used which allows to adjust the spacing between the graphite electrodes and the

mercury without stopping the operation. In this case, the anode stems are fixed to the cover by means of special stuffing boxes and sealed with rubber rings. Each stem is fastened in a cast iron socket by two set screws, along which it can be vertically moved when needed. The bottom surface of the anodes is provided by suitably profiled channels, which allow the easy escape of the chlorine produced. Due to these improvements the energy consumption can be lowered.

The modern types are built for current loads up to 30.000 A. The voltage across the cell at current density of 39 A per sq. dm. is 4.25 V, and at current density of 48 A per sq. dm. about 4.5 V. Current efficiency is about 95 %. Energy consumption for 100 kg of NaOH produced is about 300 kw-hr. at current density of 39 A per sq. dm. and about 320 kw-hr. at current density of 48 A per sq. dm.

γ) Preparation of brine for electrolytic manufacture of chlorine and caustics

The electrolyzers producing sodium hydroxide are fed with saturated brine (300 to 310 NaCl per litre), which is prepared in most works by dissolving common salt. In mercury electrolyzers, the salt is dissolved in the spent brine which as a rule is set free from the dissolved chlorine, and which contains after leaving the electrolyzer 260 to 280 g NaCl per litre. With the diaphragm electrolyzers, which yield a caustic solution containing 120 g NaOH and 200 g NaCl per litre, the so called return solution is added to the brine prepared by dissolving the salt. This return solution is obtained in a later stage of the process in the course of evaporation of the caustic solutions.

The manufacture of potassium hydroxide by the diaphragm methode starts from a solution containing some 370 g KCl per litre; the hydroxide solution thus obtained will contain some 180 g KOH per litre. The amalgam electrolysis uses a solution containing 350 g KCl per litre, the depleted spent brine usually contains about 290 g KCl per litre.

Before the saturated brine is introduced into the electrolyzer, the major part of the present magnesium and calcium salts as well as sulphates must be removed. In the diaphragm electrolysis, a larger quantity of magnesium or calcium salts is undesirable because they would be precipitated in the alkaline solution and clog the diaphragm pores. For the mercury electrolysis, the removal of calcium and particularly iron and magnesium is even more important, because their presence facilitates the discharge of hydrogen cations at the mercury electrode. With either of these electrolytical methods a higher content of sulphates (above 10 g of Na_2SO_4 per litre) is undesirable as it promotes the evolution of oxygen at the anode and at the same time increases the consumption of graphite. In course of the amalgam electrolysis the sulphate is removed by precipitation as barium sulphate. Diaphragm electrolysis does not require precipitation as the sulphates are removed from the brine in the final stage of the process during the evapora-

tion of the caustic solution. Here the sulphates are separated in the form of a poor soluble triple salt Na_2SO_4 . NaCl . NaOH.

The technological process for purifying brine is almost identical with both diaphragm and mercury cell methods of the manufacture of either sodium or potassium hydroxide. Therefore, it is sufficient to describe only the preparation of brine in the manufacture of sodium caustic by the amalgam method.

In the past, salt was dissolved in concrete or iron vessels, lined with rubber and ceramic tiles, while today brine is prepared in modern plants in large bunkers made of reinforced concrete. The spent brine, previously freed of the dissolved chlorine, is sprayed directly onto the salt carried from the store by a transporter to the bunker. The quantity of sodium hydroxide necessary to precipitate magnesium and iron in the form of their hydroxides is added to the brine at 50 °C, before it is resaturated with the solid salt. The saturated brine runs from the bunker through a concrete channel into iron storage tanks lined with acid proof bricks where it is stirred by a rubber-lined agitator in order to dissolve all the salt crystals carried with. The brine is then pumped into iron precipitating vessels lined with stoneware where it is agitated mechanically or by means of air. Calcium is precipitated by soda and sulphate ions are precipitated by barium chloride solution. Sometimes impurities are removed by adding a suspension of barium carbonate to the brine which also contains the required amount of soda. During precipitation, which is analytically checked, care must be taken that the purified brine does not contain any free barium chloride and retains some sulphate ions and a slight amount of calcium. The brine must not contain any heavy metals (Fe, Cr, V, Mo, Ti). Final alkalinity should reach some 0.08 g NaOH per litre. Recently it has been found that chlorate formation can be reduced and the life of the graphite electrodes extended if the brine is acidified by hydrochloric acid to reach pH — 3—4, after the ions Mg^{++}, Ca^{++} and SO_4^{--} have been removed.

The treated brine is then pumped, either directly or, after the main part of the precipitate has settled in large settling tanks, to the filter station. Filtration was previously carried out in filter presses equipped with polyvinylchloride filter cloths. At present Kelly filters are used and the clear liquor flows to large pure brine storage tanks, made of concrete, lined with plastic (oppanol) and bricked with stoneware plates. From the tanks the brine is pumped through small Kelly filters into overflow containers. Here the brine is maintained at constant level, so that the liquid under constant hydrostatic pressure flows into the individual electrolyzers. The saturated and perfectly purified brine entering the mercury electrolyzers should have the following approximate composition:

Na Cl	300 - 310 g/l
Na_2SO_4	2 - 10 g/l
Na Cl O_3	2 – 5 g/l
Mg max.	3 mg/l
Ca max.	10 – 100 mg/l
Fe max.	1 mg/l
pH	3 – 9

Particular attention must be paid to the purification of brine when manufacturing potassium hydroxide, as potassium amalgam is much more sensitive to impurities (Mg, Ca, heavy metals) than sodium amalgam.

When the brine leaves the electrolyzer it has a lower content of chloride and contains also dissolved chlorine and a certain amount of hydrochlorous acid. Chlorine makes working conditions difficult, particularly when the salt is dissolved in open tanks, and attacks the iron part of the equipment. For this reason the brine must be dechlorinated prior to resaturation and simultaneously cooled. When saturation has been completed and the brine enters the electrolyzer, the temperature should not exceed 50° to 60 °C. In winter when the temperature has dropped below 50 °C the brine must be heated.

The spent brine runs through rubber-lined pipings from all the electrolyzers to a collecting tank which is coated with rubber and lined with acid proof tiles. In the tank, a 30 per cent solution of HCl is added sufficient to obtain acidity equalling about pH = 2.2. With this degree of acidity hypochlorous acid and a certain amount of chlorate will be decomposed into chlorine and water. In the course of this process a small amount of chlorine is set free in gaseous form which is conducted from the collecting tanks into the chlorine main manifolds. The brine is then pumped by stoneware pumps into two iron, rubber-lined vessels, filled with Raschig rings. Here under a vacuum of some 400 mm Hg, the amount of dissolved chlorine is lowered — by desorption from the original contents of 0.5 g — to 0.1 g per litre. A stoneware liquid-piston type rotary air pump maintaining a vacuum in the equipment pumps the freed chlorine through a cooler and a separator of condensed water vapour into the chlorine main. The brine freed of most of the chlorine runs out of the dechlorination vessels through a barometric leg and a liquid seal. It is then pumped to the top of rubber-lined towers, where further chlorine is expelled by blowing air, which reduces the chlorine content to around 0.01 gram per litre. The small remnants of the chlorine are removed from the brine by an admixture of sodium bisulphite ($NaHSO_3$) or sulphur dioxide. If necessary, dechlorinated brine is then cooled in a vacuum cooling tower. Here the vacuum necessary to cool the solution by evaporation is attained by a steam ejector. Then the brine, cooled to 50 °C, is pumped by pumps for resaturation. Before the brine enters the suction branch of the pump a sodium hydroxide solution is added to it through a branch pipe. Both liquids are thoroughly mixed in the pump.

Another method can be used to remove the chlorine from the brine which is based on the following reactions:

$$Cl_2 + 2\,OH^- = ClO^- + Cl^- + H_2O \qquad \text{(XI-36)}$$

$$2\,ClO^- + C = CO_2 + 2\,Cl^-. \qquad \text{(XI-37)}$$

Purification is carried out by adding to the spent brine a sufficient quantity of alkali hydroxide to convert the free chlorine into hypochlorite (XI-36). The brine (at 60 to 80 °C) is then led to the bottom of the towers which are filled

with lumps of graphite from used anodes, and leaves from the top almost free of chlorine (XI-37).

This dechlorination method is not considerably applied in practice as it entails the consumption of a certain amount of alkali hydroxide and also all the dissolved chlorine is depreciated by conversion to chloride. Therefore, this method is sometimes used for removing the last remnants of chlorine from the brine which has previously been dechlorinated by evacuation and aeration instead of the method using sodium bisulphite and sulphur dioxide because in this case undesirable sulphate ions are formed in the brine.

When removing chlorine from the brine more hygienic working conditions are conduced and operations facilitated, as cast iron or steel pumps, vessels and manifolds not protected by rubber lining may be used.

c) *Further Treatment of Products of the Alkali Chloride Electrolysis*

α) Treatment of Electrolytic Chlorine

All chlorine is sucked from the bath by a rubber-lined air-blower under a vacuum of 10 to 20 mm of water column. It is first led by a rubber-lined piping into two cooling boxes (connected in series) through which stoneware coils pass. Cooling water flows through the latter. In the boxes, the gas is cooled down to some 20 °C. Cooling below 10 °C is not permissible for at a lower temperature solide hydrate $Cl_2 . 8 H_2O$ can be formed. After cooling, chlorine is washed in a tower packed with Raschig rings by circulating water, in order to remove the brine mist entrained. Wash water saturated with chlorine is led into the dechlorination department, or else directly to a sewer.

The cooled and washed gas is then dried by scrubbing with strong sulphuric acid in two drying towers made of stoneware or steel, coated with oppanol and acid proof tiles and packed with Raschig rings. Concentrated (96 per cent) sulphuric acid is first circulated through the second tower, and after its concentration has dropped to 90 per cent, it is pumped into the first tower. Here it is circulated again until it is diluted to 80 per cent, to be replaced thereafter by new acid. Both towers are provided with an acid cooling equipment. The acid is kept circulating by pumps made of ferro-silicon.

Ultimately the dry chlorine (generally containing some 1.4 g H_2O per cu. m.) is filtered through a 30 cm high layer of quartz or coke to remove the droplets of sulphuric acid. It is then collected in a gas holder or led to a compressor station where liquid chlorine is produced. Dry gas will not corrode steel so it can be led through nonprotected steel piping. As the whole drying process is carried out under a vacuum the chlorine will be slightly diluted with air, concentration will drop from 95—97 per cent to 92—93 per cent, this depending on the tightness of the piping.

Liquid chlorine

The critical temperature of chlorine is 144°C and its critical pressure is 76.1 atm. Boiling point of liquid chlorine is — 34.6 °C. Thus chlorine is normally below its critical temperature and can be liquefied either by compression or by refrigeration. Usually a combined method is used i. e. compression to a medium pressure and suitable cooling.

If pure chlorine is to be liquefied at a constant temperature, it must be compressed to a pressure equalling the equilibrium vapour pressure of the liquid chlorine at the same temperature. The evolved condensation heat must be then lead away. If the chlorine is not entirely pure, compression must be increased by partial pressure of all inert gases. If chlorine containing other gases which cannot be liquefied readily is compressed it will be liquefied alone and its concentration in the gas phase will be decreased. Should further portions of chlorine be liquefied it would be necessary to increase the pressure in proportion to the increasing concentration of the inert gases in the gas phase.

In practice, however, the operation is not carried out at constant temperature, but it is convenient to compress the gas to a definite final pressure prior to its gradual cooling to lower temperatures. It can be understood that after the gas has passed through the last stage of cooling it still contains a certain amount of chlorine which depends upon the composition of the gas in the initial state and upon the working conditions.

From the dependence of vapour tension on temperature it follows that liquefaction of pure chlorine requires the gas to be cooled to — 1 °C under a pressure of 3.5 atm. or to — 10 °C under a pressure of 2.7 atm. or else to — 30 °C under a pressure of 1.3 atm. If, however, chlorine containing impurities is liquefied by cooling in steps a certain part of gas will be liquefied at each step, whereupon partial pressure in the remaining gas will drop to equilibrium pressure corresponding to the given temperature. Consequently, if gas compressed to 7 atm. passes through a system of coolers, the temperature of the last of them is — 10 °C, the quantity of chlorine retained in the gas corresponds to the equilibrium pressure of saturated chlorine vapour equalling 2.6 atm. (i. e. $100 \times 2.6/7 = 37$ per cent). Hence, if the liquefaction process is completed under similar conditions, approximately one volume of chlorine is lost in the discarded gas to every two volumes of inert gases.

With regard to liquefaction, particular attention must be paid to the presence of hydrogen, which if reaching higher proportions may cause an explosion. In order to eliminate this risk, only such a portion of the total amount of chlorine will be liquefied to keep the concentration of hydrogen in the tail gas leaving the condenser after liquefaction within 4 per cent. Should the gas in the initial state contain e. g. 0.5 per cent hydrogen it would be not possible to liquefy, more than 90 per cent of the gas, as the hydrogen content in the non-condensed gas must not to exceed the limit stated above. However, such tail gas is still rich in chlorine and contains approximately 4 per cent H_2, 12 per cent CO_2,

16 per cent air and 68 per cent Cl_2. It is used for the manufacture of chemicals such as hydrochloric acid, alkali hypochlorites, and for the chlorination of organic substances.

In certain works chlorine contains a greater amount of hydrogen (i. e. more than 1.0 per cent) which is removed before drying with sulphuric acid is carried out. Hydrogen is allowed to react with chlorine to hydrogen chloride which is then absorbed in water in an absorption tower. The operation is carried out in a lead-lined iron cylinder which contains many vertical quartz tubes equipped with silicon carbide heating rods or metal resistance wires. Chlorine being led upwards around the tubes is heated up to 300 °C, while it combines with hydrogen. In this way the hydrogen content can be reduced to 0.1 — 0.2 per cent. It is evident that chlorine freed of hydrogen prior to treatment gives a higher yield when liquefied, and the tail gases are by far poorer in chlorine than they would be if the chlorine had not been previously purified.

A disadvantage of this method is that a certain amount of chlorine depreciates to hydrochloric acid. For this reason, care should be taken that the chlorine on leaving the electrolyzers contains as little hydrogen as possible (below 0.3 per cent).

In practice, three liquefying methods are used. The first liquefies the chlorine by compressing the gas to a pressure of 10 to 12 atm. and cooling it by water. The second is a combination of medium pressure of approximately 6 to 7 atm. with ultimate cooling to — 10 °C. The third compresses the chlorine to a pressure of about 0.3 atm. then subjects it to drastic cooling to — 40 °C. The advantage of the last methode is that no high pressure compressors requiring a careful maintenance are needed. On the other hand, the cost of this refrigerating equipment is high and perfect thermal insulation requirements are not easy to comply with.

Previously, in the initial stages of the manufacture of liquid chlorine, difficulties arose regarding the lubrication of compressors as chlorine causes all kinds of oils to change into a gummy substance. Also gaseous hydrogen chloride is evolved which corrodes the equipment. These difficulties were overcome when concentrated sulphuric acid was found to be a suitable lubricant. At present, compressors are also made with graphite piston rings which do not require lubrication.

Liquefaction by medium pressure (compression to 6—7 atm.) is obtained by two-stage vertical compressors made of special cast iron with water cooling and lubrication with concentrated sulphuric acid. The crankshaft of the compressor is located above the pistons. The compressors are built for a capacity of 5 000—40 000 kg of chlorine per day. Compression takes place in two stages. At first the gas is compressed to 1.5—2 atm. overpressure. The gas heated by the compression to some 80 °C*) is led through a sulphuric acid separator. Sulphuric

*) In order to prevent any corrosion that would occur above this temperature the gas is sometimes cooled by an injection of a small amount of liquid chlorine before entering the compressor.

acid which has penetrated into the gas from the compressor is here separated and the gas led into a water cooler. The cooled chlorine is brought to a pressure vessel, from where it is sucked into the second stage of the compressor and compressed to 6—7 atm. The compressed gas freed again from the entrained sulphuric acid enters through iron piping a series of mutually connected condensers. The first of them are cooled with water to about 20 °C, the rest is cooled to — 10 °C with brine which in turn has been cooled by liquid ammonia. In these condensers the compressed chlorine passes through coils and is gradually liquefied. The coil is made of a pipe 50 mm in diameter which adheres to the walls of the container. At the lower end of the container this outer spiral is connected to a second coil which consists of a pipe 80 mm in diameter wound concentrically with the first coil and runs out at the top edge of the container. Compressed chlorine entering the 50 mm diameter coil is partly liquefied and flows out at the lower end into iron receivers. Through the wider coil, uncondensed gases flow upwards, leaving the coils at its top end.

With some equipments also single coils are used for cooling. Liquid chlorine with the noncondensed gases is led into the liquid chlorine receiver, from where the discard chlorine is gradually let out.

First of all liquid chlorine is measured in a pulsometer, then collected in a liquid chlorine receiver equipped with a safety valve as a safeguard against increased pressure. Outside, it is insulated with cork to keep the temperature as low as possible. The volume of the receiver usually amounts to 20 cu. m. The liquid chlorine is pumped by means of air, compressed to 12 atm. and dried with concentrated sulphuric acid or silicagel.

Liquid chlorine is shipped either in 14.5, 36 or 54 ton tank cars, or in 600 kg steel barrels or in 42 kg steel cylinders. In these containers the chlorine is kept at 20 °C under 6.6 atm. The volume of the vessels must not be utilised beyond the limit of 80 per cent. 1 kg of liquid chlorine occupies a volume of 0.8 l and after vaporization will yield 317 litres of gas.

Pressure storage tanks and shipping containers must have periodical pressure tests and inspection according to strict regulations.

Today, liquid chlorine has often superseded bleaching powder and sodium hypochlorite, for although its packing is weighty, the transport cost is lower than with either of the other compounds. The ballast which must be transported with the two other compounds is relatively even higher than with chlorine (1 kg of liquid chlorine yields 317 l gas while 1 kg of bleaching powder of 35.5 per cent active chlorine yields only 112.6 l of gaseous chlorine). A bleaching agent can be made of liquid chlorine on the spot, where needed.

β) Treatment of electrolytical hydrogen

Hydrogen freed in the electrolyzer is sucked off by a liquid-piston type rotary blower and led under slight overpressure of 10 to 15 mm water column through an iron manifold to tubular water coolers, in which the temperature will drop from some 70—75 °C to 25 °C. From the cooler, the gas passes either directly

to the place of consumption or it will be, especially in winter, dried in two towers, connected in series, in which the concentrated sulphuric acid flows down the packing of Raschig rings. After leaving the tower the acid is cooled in a heat exchanger and recirculated. As soon as its concentration has dropped to 90 per cent H_2SO_4 it is replaced by a fresh supply. In some works, hydrogen is dried with solid potassium hydroxide.

Hydrogen escaping from a diaphragm electrolyzer is purified in this way, and can be used for chemical or other purposes, i. e. hydrogenation, the manufacture of ammonia or to produce compressed hydrogen etc.

Hydrogen which is evolved in an amalgam electrolyzer entrains a considerable amount of mercury vapour (approx. 50 to 80 mg per cu. m) from the denuder. This vapour not unfrequently prevents further utilization of the hydrogen.

When being cooled in tubular coolers part of the mercury vapour is condensed and the separated mercury is caught in a separator connected with the cooler. After drying with sulphuric acid, hydrogen which now contains 20 to 30 mg of mercury per cu. m. is led for further condensation of the mercury vapour to a condenser cooled by the evaporation of liquid ammonia to — 45 °C. The gas is then filtered by passing through cotton and a layer of activated carbon. The purified hydrogen contains only 0.001 mg of mercury per cu. m.

Mercury can be also chemically removed from hydrogen. The gas, cooled to 25 °C in a tubular cooler passes through three rubber-lined towers in series. In the first it is washed with partly dechlorinated brine which contains some 0.01 to 0.02 g of chlorine per litre. The chloride formed by the reaction between chlorine and mercury is washed with water from the hydrogen in the second tower which is packed with coke. A small amount of sulphur dioxide is added to the gas to remove the excessive chlorine and the hydrogen is led to a third tower, in which it passes through a layer of active carbon. Hydrogen purified in this way contains around 0.01 mg Hg per cu. m. If dry hydrogen is required it is finally dried by washing with concentrated sulphuric acid.

γ) Caustic solution treatment

In a mercury cathode electrolyzer a pure caustic solution containing some 50 per cent NaOH can be produced without any difficulty while in a modern diaphragm electrolyzer the caustic solution contains on an average no more than 100 to 135 g NaOH, besides 180 to 200 g NaCl per litre. Because of the presence of salt such a solution cannot be utilized while the high degree of dilution increases the cost of transportation. For these reasons it is concentrated in evaporators to a 50 per cent caustic solution. During this process the sodium chloride which in a concentrated caustic solution is less soluble crystallizes and can be removed by filtration. In a 50 per cent caustic solution, at 20 °C, only 1.8 per cent NaCl dissolves, calculated in relation to the 100 per cent NaOH. Actually a little more salt (2—3 %) is left in the caustic solution, calculated on the basis of 100 per cent NaOH, as, owing to a high viscosity of

the solution, it is difficult to remove entirely the fine salt crystals by means of filtration. (In a concentrated potassium hydroxide solution, 1.7 to 2 per cent KCl is left, in relation to 100 per cent KOH.)

The concentration of caustic solution by evaporation is a problem not easy to solve. First of all, caustic solutions have an elevated boiling point which reduces the difference between the heating steam temperature and the boiling point of the solution to be evaporated. The evaporating efficiency of multiple-effect evaporators is, therefore, lowered. Also the heat transfer coefficient is rather low for more concentrated and viscous solutions. Many difficulties arise because of the corrosive effect of caustic solutions on steel, which causes it to become brittle. Nickel is the only technical metal that resists the corrosive effect of caustic solutions and does not become brittle. But nickel is too expensive to use in the construction of evaporators with a natural circulation of the liquid. Only when high efficiency evaporators have been constructed, based on the principle of forced circulation of the liquid where the heat transfer coefficient is four to five times higher and the heating surface smaller in the same proportion, the use of nickel is economically justified. However, even for this type of evaporator the heating tubes alone are made of nickel, whilst the body is usually made of cast iron, which resists caustic solutions quite satisfactorily. Only wherever a particularly high degree of purity is required, the body of the evaporator is made of nickel-clad steel and the heating tubes, the piping and the circulation pumps are made of pure nickel.

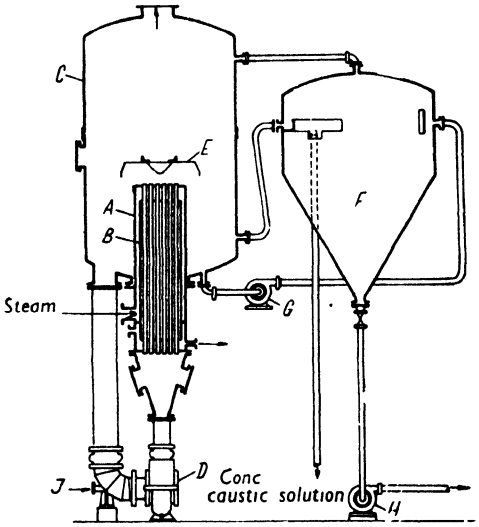


Fig. 106. Forced circulation caustic solution evaporator.

A — heating element with nickel tubes, *B* — baffle leading steam to the top of the heating element then along the heating tubes, *C* — evaporator body, *D* — caustic solution circulating pump, *E* — deflector to catch entrained droplets, *F* — settler, for settling salt precipitated from the evaporated caustic solution, *G* — pump transporting thin salt slurry into the decanter, *F*, *H* — pump transporting thickened salt slurry to the filters, *J* — caustic solution feed to the evaporator.

An evaporator with a forced circulation of the liquid and a barometric condensation is shown in Fig. 106. Here, *A* is the heating element with nickel tubes, provided with steam supply connections and outlets for the condensate and noncondensable gases. The heating element projects about one half of its length into the body of the evaporator *C*, which is connected at the lower end by a wide pipe to the pump *D*. Fresh caustic solution, preheated in the heat

exchanger by the steam condensate from the evaporator to some 90 °C, is introduced by a pipe branch just before the pump. The solution level in the evaporator body *C* is maintained below the top end of the heating element *A*. Caustic solution droplets, entrained in the evolving vapour, are caught by deflector *E*. The speed of the liquid circulated through the evaporator by the circulating pump *D* reaches approx. 3 m per second. The salt precipitated in the course of evaporation of the solution is removed by withdrawing a certain amount of the liquid by the pump *G* to the settling vessel *F*. Oppositely to the liquid inlet an overflow is located, which collects the clear solution. A part of the solution gravitates back to the evaporator and another part is withdrawn as the evaporated caustic solution. The thickened salt slurry, sedimented in the cone bottom of the settler *F*, is pumped by means of pump *H* to the filters.

Electrolytic hydroxide is, as a rule, concentrated to 50 per cent NaOH. Multiple-effect evaporators which work in steps are used for this purpose. For technical and economical reasons the process is carried out in two stages. In the first a double- or a triple-effect evaporator is used and the solution is evaporated up to 30 to 35 per cent NaOH. The first effect is usually operated under overpressure which amounts to 0.7 atm., the second and the third effects operate under a vacuum, which reaches 350 mm Hg in the second and 670 mm Hg in the third effect respectively. Vapours from the first effect are led as heating steam to the second effect and vapours from the second effect pass to the third effect. The vapour from the third effect is led into a barometric condenser, with a barometric leg and seal. The salt retained in the settling vessels of the individual elements is separated in suction filters, in rotary vacuum filters or in centrifuges. The salt is washed with water to remove all the caustic and is then dissolved to a saturated brine which is returned as the so called return solution into the process of the electrolysis. A partially evaporated caustic solution from the last element of a multiple-effect evaporator must pass through a settling tank, so that the minute particles of salt settle. The clarified solution is pumped from a storage tank to a single-effect final evaporator of the second stage. This evaporator is heated by the vapour from the first stage and so operated under a vacuum of 680 mm Hg. In the final single-effect evaporator the caustic solution is concentrated to 50 per cent NaOH.

Evaporated solution is then pumped into the stirred continually operating crystallizers where it is cooled from 90° to 25 °C. All impurities and salt crystals are then allowed to separate in settling vessels. The clear solution is afterwards pumped into storage tanks, where a small amount of sodium hypochlorite is added in order to decolorize the lye.

Thin slurry separated in settling vessels is then centrifuged from the remaining solution. The crystals so gained which contain mainly a triple salt $Na_2SO_4 \cdot NaCl \cdot NaOH$, are freed from sodium hydroxide by washing with water.

The 50 per cent caustic solution obtained by evaporation of the diaphragm cell liquor meets the current industrial requirements. For the manufacture of rayon, one of the foremost industries today, the salt content of the diaphragm

liquor is far too high. Therefore other methods of purifying caustic are applied. (Caustic manufactured in a mercury electrolyzer is sufficiently pure, and so no further purification is necessary).

According to one of the methods, a 50 % caustic solution is first diluted to an approximately 35 % solution and cooled to 5 to 15 °C. In course of the slow cooling various hydrates crystallize — $NaOH \cdot 2\,H_2O$, $NaOH \cdot 3.5\,H_2O$ and $NaOH \cdot 4\,H_2O$, according to temperature and degree of dilution. The separated crystals are then centrifuged from the mother liquor, in which a major part of the sodium chloride and other impurities remain. The crystals are then melted and the solution is once again concentrated to a 50 per cent NaOH product. This process entails high operating cost, arising from the cooling and evaporation of the solutions, but yields a sufficiently pure product (0.2 to 0.3 per cent NaCl, related to 100 per cent NaOH basis).

The basic feature of the second method consists in the separation of the triple salt $NaCl \cdot Na_2SO_4 \cdot NaOH$ which is poorly soluble. In this process about 50 g of anhydrous sodium sulphate is added to 1 litre of the caustic solution. Through cooling and settling, salt of a composition given before is separated. Clear caustic solution will then contain 0.2 to 0.6 per cent NaCl, related to 100 per cent NaOH basis.

The purest caustic solution is obtained by extraction with ammonia. The initial 50 per cent caustic solution is led to the top of an extraction tower and flows countercurrently to a mixture of 75 per cent ammonia and 25 per cent water which rises from below. The two solutions are immiscible. The ammonia solution extracts almost completely the chloride and sodium chlorate from the caustic liquor so as to leave no more than 0.08 per cent NaCl (related to 100 per cent NaOH) and practically no chlorate. Ammonia regeneration equipment complements the extraction unit. If anhydrous liquid ammonia is used instead of an ammonia solution a certain degree of concentration of the caustic solution can be achieved at the same time as ammonia also extracts water from the caustic solution.

A 50 per cent NaOH solution, either produced directly in a mercury electrolyzer, or in a diaphragm electrolyzer subsequent to preliminary evaporation, is shipped in normal 57 or 17 ton tank cars, in 600 kg steel drums or in 50 kg glass carboys.

The preparation of fused anhydrous alkali hydroxides

When manufacturing solid sodium hydroxide on industrial scale a caustic solution containing 50 per cent NaOH is evaporated. This is either done directly into the final product or by an intermediate concentration to a 75 per cent NaOH solution. For intermediate concentration a standard single-effect vacuum evaporator is used. As no salt is separated in the course of this evaporation process, the design of the evaporator is very simple. All pumps as well as the piping must be steam jacketed to prevent the solidification of the highly concentrated liquor.

Table 16. Czechoslovak standards for sodium hydroxide

	Sodium hydroxide solutions		Fused sodium hydroxide				
	Grade „S" %	Grade „N" %	Technical grade %	Special grade %	Purissimum „chem. pure" %	Purum "p. a." %	Depuratum "purum" %
Total alkalinity as NaOH min.	42	41,5	98	99	96	96	96
NaOH min.	—	—	97	98	—	—	—
Na_2CO_3 max.	0,5	1,2	1,5	1,0	1,0	1,5	4
Cl^- max.	0,01	0,013	0,6	0,3	0,005	0,005	0,025
Fe max.	0,0003	0,002	0,02	0,01	0,0005	0,001	0,002
SO_4^{--} max.	—	—	—	—	0,005	0,003	0,03
SiO_2 max.	—	—	—	—	0,01	0,01	0,1
PO_4^{---} max.	—	—	—	—	0,003	0,005	0,01
N max.	—	—	—	—	0,001	0,001	0,001
Heavy metals	—	—	—	—	0,003	0,003	0,003
Ca max.	—	—	—	—	0,012	0,024	0,06
R_2O_3 max.	—	—	—	—	0,0015	0,0015	0,015

Table 16a. Czechoslovak standards for potassium hydroxide

	Potassium hydroxide solutions	Fused potassium hydroxide			
	%	Technical grade %	Purissimum "chem. pure" %	Purum "p. a." %	Depuratum "pure" %
Total alkalinity as KOH min.	37	90	—	—	—
KOH min.	—	88	—	—	—
K_2CO_3 max.	5	2,5	1	1,5	2,0
Cl^- max.	0,07	0,5	0,005	0,004	0,008
Fe max.	0,015	0,03	0,0005	0,0005	0,0008
SO_4^{--} max.	—	—	0,005	0,002	0,003
SiO_2 max.	—	—	0,01	0,005	0,01
PO_4^{---} max.	—	—	0,003	0,002	0,006
N max.	—	—	0,001	0,001	0,002
Heavy metals	—	—	0,003	0,001	0,002
Ca max.	—	—	0,006	0,001	0,003
R_2O_3 max.	—	—	0,01	0,002	0,003

To remove the remaining water, it is necessary to heat the 75 per cent sodium hydroxide in caustic melting pots over a direct fire. As sodium hydroxide melts at 318 °C, the temperature in the fire-box must reach 450 to 500 °C, in order to drive off even the last remnants of water. The manufacture of solid product directly from a 50 per cent caustic solution is carried out in the same equipment.

The cast iron melting pots are hemispherical in shape. For 20 tons of caustic solution, a vessel 1800 mm deep and 3000 mm in diameter is needed (see Fig. 107).

The pots are mounted on brickwork and heated by generator gas, coal or oil. The flames are not in direct contact with the wall of the pot, but the flue gases must circulate around it in order to lengthen the life of pots. Generally, there are two pots mounted in one fire-box, one for melting and the other for preheating the caustic solution. The first pot is the lower one and is heated by the flue gas from the fire-box. From beneath this pot, the gases are led around the other pot. The melting process takes 3 to 4 days. In order to make the process more economical, a multiple cascade is sometimes used for direct concentration of a 50 per cent caustic solution which passes from one pot to another.

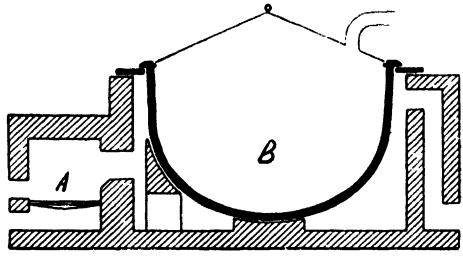


Fig. 107. Caustic melting pot.
A — fire-box, *B* — pot.

The high temperature of the flue gases, the uneven heating of the pots and also the corrosive effect of the caustic cause the cast iron pots to wear out rather

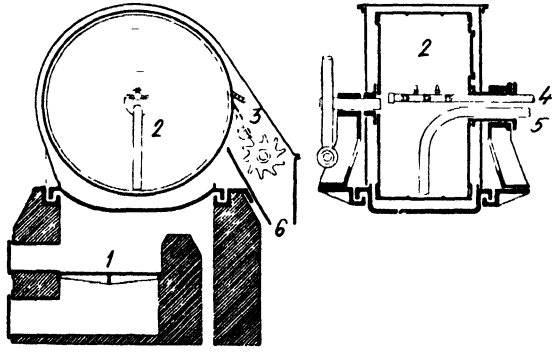


Fig. 108. Flaking drum.
1 — fire-box, *2* — water cooled rotating drum, *3* — scraping device, *4* — cold water inlet, *5* — hot water outlet, *6* — hydroxide flakes discharge.

quickly; usually after one hundred melting operations the pots are burnt through or burst. Better resistance is found with pots made of cast iron with an admixture of 3 per cent nickel. The best of all are inside nickel coated iron pots, which are very expensive. (Nickel pots would burst because of the presence of sulphur compounds in the flue gas).

In order to make the walls of the iron pot passive a small amount of alkali chlorate (some 20 kg per 8 000 kg of caustic) is added to the melt. The iron which in spite of this measure dissolves in the caustic in the form of sodium ferrate $Fe(ONa)_3$, is reduced by an admixture of sulphur to give ferrous sulphide which is separated by settling together with other impurities, especially sodium carbonate. The melt is left standing and cooled to 350 °C. It is then siphoned or pumped by an immersion pump directly to iron drums where it solidifies. Flaked hydroxide can be also obtained if a water cooled rotating drum is dipped into the melt. A thin film of hydroxide will adhere to the rotating drum. The film solidifies and is scraped off with a thin knife. (See Fig. 108.)

The solidified residue at the bottom of the pot is broken to pieces and dissolved in water. Then the solution is filtered and added to fresh lye for melting.

Melted sodium hydroxide is yellowish or bluish in colour and may contain up to 99.5 per cent NaOH when manufactured from a caustic solution produced by amalgam electrolysis. Diaphragm manufactured hydroxide is less pure. Sometimes the NaOH content is given in °C. S. (Carbonate de Soude), then 130 °C. S. equals 98 per cent NaOH.

Potassium hydroxide is treated in a similar way but due to its higher aggressivity, it is evaporated to a maximum of 90 to 92 per cent. Then it is filled directly into drums or, after being solidified, is broken up into pieces varying from the size of a walnut to the size of a fist.

XII. HYDROGEN CHLORIDE AND HYDROCHLORIC ACID

Hydrogen chloride is a colourless and poisonous gas with an acid taste and fuming in air. It is relatively stable. Thermal decomposition sets only above 1700 °C. Its critical temperature is 51.3 °C, its critical pressure equals 81.6 atm.; for this reason it liquefies easily (e. g. at 10 °C under 40 atm., at 0 °C under 26.2 atm.). Under a pressure of 1 atm., the boiling point of liquid hydrogen chloride is — 83 °C and the freezing point — 111 °C.

Hydrogen chloride dissolves in water releasing heat Thus hypochloric acid is formed. At 18 °C, its saturated solution contains 42.3 per cent HCl. The azeotropic mixture containing 20.24 per cent HCl has a boiling point 110 °C at 1 atm. pressure.

Large amounts of hydrogen chloride are prepared by the combustion of hydrogen in chlorine gas. For this reason, the manufacture of hydrochloric acid is usually a by-production of the electrolysis of alkali chlorides. Another method of manufacturing hydrogen chloride consists in decomposing sodium chloride with sulphuric acid (or gases from roasting pyrites), sodium sulphate being a by-product of this process. Smaller amounts of hydrogen chloride are formed as a by-product in certain chemical processes (particularly in the course of chlorination of organic substances).

A. THE PRODUCTION OF HYDROGEN CHLORIDE

1. The manufacture of hydrogen chloride by the decomposition of sodium chloride with sulphuric acid

Formerly, hydrogen chloride was produced as a by-product of the first stage of the Leblanc soda ash process, based on the reaction:

$$2\,NaCl + H_2SO_4 = Na_2SO_4 + 2\,HCl. \qquad \text{(XII-1)}$$

The Leblanc process has been given up but decomposition of sodium chloride with sulphuric acid has not been abandoned, as a way has been found to utilize the by-product of this reaction, i. e. sodium sulphate, in the glass industry and other industries.

Actually, the decomposition of sodium chloride is not so simple as it may appear from the equation (XII-1) as several kinds of acid salts are formed as the intermediary phases, which while being heated are ultimately converted into anhydrous sulphate. In order to simplify the problem we assume the existence of the acid sodium sulphate $NaHSO_4$ as the sole intermediary phase, so the total reaction (XII-1) can then be divided into two steps:

$$NaCl_{(s)} + H_2SO_{4(l)} = NaHSO_{4(l)} + HCl_{(g)};\ \Delta H^\circ_{291} = 0.79\ \text{kcal}, \qquad \text{(XII-2)}$$

$$NaCl_{(s)} + NaHSO_{4(l)} = Na_2SO_{4(s)} + HCl_{(g)};\ \Delta H^\circ_{291} = 14.89\ \text{kcal}. \qquad \text{(XII-3)}$$

Whilst the first reaction only requires a small amount of heat, the second reaction is strongly endothermic. Since two solid phases (NaCl, Na_2SO_4), one liquid phase (Na HSO_4) and one gaseous phase (HCl) participate in the process, at a given temperature the equilibrium is defined by the partial pressure of the hydrogen chloride only. The pressure pertinent to the first reaction reaches a very high value already at a normal temperature so that the formation of bisulphate may be regarded as a process proceeding to completion in the course of which all sodium chloride will be consumed. On the other hand, the reaction which occurs according to the second equation will require a higher temperature so that the partial pressure of the evolving hydrogen chloride is able to surmount the pressure of the ambient atmosphere. Practice has proved the necessity of raising the temperature to 460 °C in this stage of the process so that the reaction proceeds with a sufficient rate and the contamination of the solid product with $NaHSO_4$ is prevented.

As the process takes place between a liquid and a solid substance the rate of the reaction depends, apart from the temperature, on the size of the contact surface of the reacting substances. For this reason, it is necessary to make sure that a thorough mixing takes place which should not be particularly difficult in the first stage as the reacting mixture is sufficiently thin. In the second stage, the fused acid sulphate reacts with the solid sodium chloride to solid sodium sulphate which makes the reaction mixture very viscous.

In the older type of furnaces sulphuric acid 60 °Bé (78 per cent H_2SO_4) was used. Modern mechanical furnaces work with a concentrated acid of 93 to 96 per cent H_2SO_4 to prevent the dilution of the hydrogen chloride with water vapour as this would hamper the manufacture of concentrated hydrochloric acid. Apart from this, diluted sulphuric acid introduces water into the process and the heat required for the evaporation of this water would increase the overall consumption of heat in the reaction.

Another necessary raw material is the sodium chloride. It should not contain too much of calcium and magnesium salts and of iron oxides.

The former salts reduce the fusibility of the reaction mixture and cause the formation of lumps which may break the blades of the stirring device in the mechanical furnaces. It is also essential to choose the suitable size of the salt grain as a higher content of salt-dust will entail a considerable escape of salt into the hydrogen chloride draining piping, whilst a high content of coarse grain will cause the product to contain an increased amount of unreacted common salt.

Originally, salt was decomposed in hand-rabbled furnaces which were later replaced by mechanically operated furnaces.

a) *Manufacture of hydrogen chloride in hand-rabbled furnaces*

The equipment of the hand-operated furnaces was adapted to the two stages of the process corresponding to the equations (XII-2 and XII-3). Reaction (XII-2) was carried out in a pan. When the mixture had reached a slurry con-

sistency it was worked into the muffle, in which the reaction (XII-3) was completed at a higher temperature to obtain neutral sulphate.

The sulphate pan *A* (see Fig. 109) was a shallow dish made of fire resistant white cast iron 2500 to 3000 mm in diameter and 400 to 700 mm deep. A firebrick arch was built above the dish with a flue in the middle for the escaping hydrogen chloride. Muffle *E*, connected to the pan by a narrow channel *N* provided with a slide was 4000 to 8000 mm long and 2000 to 3000 mm wide. The bottom of the muffle consisted of large firebrick blocks. Also the roof was built of the same material but was thicker (120 to 240 mm). Its heat resistance had to be greater than that of the bottom as the muffle was heated from above.

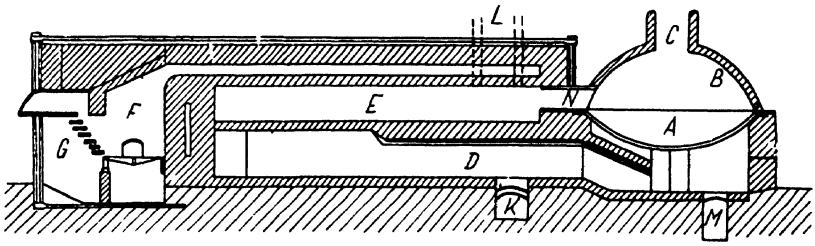


Fig. 109. Sulphate furnace.

A — white cast iron pan, *B* — firebrick arch above the pan, *C* — hydrogen chloride outlet, *D* — hot gas flues underneath the muffle, *E*, *F*, *G* — fireplace adapted as a gas producer, *K* — flue leading from the muffle into the stack, *L* — outlet of hydrogen chloride from the muffle, *M* — flue leading from pan into stack, *N* — flue connecting muffle with pan.

As reaction (XII-3) required far more heat than reaction (XII-2) the gases were first led from fireplace *F*, adapted as a gas producer above the ceiling of the muffle *E*, and descended through the vertical ports below the muffle under which they passed in two separate streams *D*, to heat the bottom of the pan and ultimately to be led into the stack. The muffle and the pan had carefully sealed operating doors to prevent hydrogen chloride from escaping into the ambient atmosphere.

Through a door in the side of the pan the salt was charged manually. Before charging, it was necessary to cool the pan and remove all the impurities remaining from the previous operation. 80 °C hot sulphuric acid was then added from a measuring tank and the batch was stirred with a long iron rod. It was imperative to maintain the required temperature in the pan for the reaction to take place properly. After the main reaction had been completed the contents of the pan were stirred by a scraper at half hour intervals, until the mixture had a pasty consistency. After the slide between the pan and the muffle had been opened the slurry was pushed manually into the muffle. Then the mixture was spread evenly on the bottom of the muffle and the slide was shut. The muffle was heated to a higher temperature than the pan but it was of the greatest importance that the melting point of the salt was not exceeded.

In order to accelerate the reaction and to complete the conversion of bisulphate into sulphate the mixture was stirred approximately every hour. Whenever clods were formed they had to be carefully crushed. When the reaction was completed the finish sulphate was raked into metal cases provided with lids and carted away. The muffle then had to be emptied and cleaned at the end of each process. One operation in the pan took 2 to $2\frac{1}{2}$ hours, so that 10 to 12 charges could be treated in 24 hours.

Hydrogen chloride escaped from the pan through pipe *C* located in the middle of the arch and from the muffle by the firebrick channel *L*, located in the sidewall. Because of leakages in the furnace more air penetrated into the hydrogen chloride in the muffle than into the hydrogen chloride in the pan. For this reason the gases were collected and absorbed in water separately as this enabled to prepare a more concentrated hydrochloric acid of the hydrogen chloride in the pan than of that which escaped from the muffle.

The furnaces yielded up to 5 000 kg of sodium sulphate per day plus the corresponding amount of hydrochloric acid. As a result of the high temperature and corrosion by the almost molten salt, construction material suffered greatly and the hydrogen chloride which escaped through the leakages made the operators work very difficult. As the work at the furnaces was very unhealthy, physically tiring and required highly skilled workers so in the course of time manually operated furnaces were replaced by mechanical furnaces and the principle of dividing the operation into two stages was abandoned.

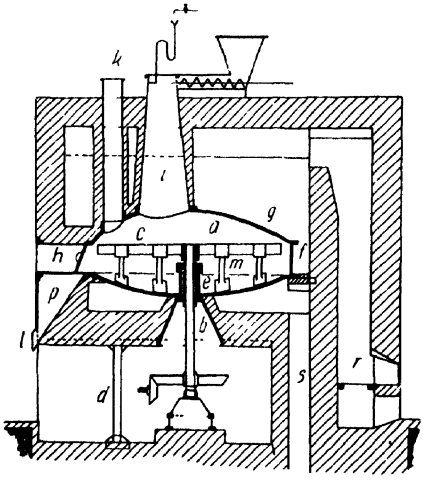


Fig. 110. Mechanical Mannheim Furnace.

a — cast iron muffle, *b* — cast iron support, *c* — stirrer, *d* — supporting structure, *h* — cleaning openings of the muffle, *i* — funnel for charging raw material, *k* — hydrogen chloride outlet, *p*, *l* — sulphate discharge, — *m* arms of stirrer, *r* — fire-place, *s* — flues into stack.

b) *Manufacture of hydrogen chloride in mechanical furnaces*

The Mannheim furnace was the first technically perfect mechanical furnace (see Fig. 110). The main feature of it is the cast iron muffle *a* and stirrer *c* with interchangeable blades. The muffle is covered with a cover *g* and rests on a cast iron support *b*, supported in turn by steel structure *d*; the drive of the stirring device is located below the muffle. The cleaning openings are in the sides of the muffle.

Originally, salt and sodium bisulphate were treated in the Mannheim furnace. Sodium bisulphate was previously a residue in the manufacture of nitric acid and was used instead of sulphuric acid. Ground bisulphate was mixed with salt

and continually fed by a worm through a funnel *i* into the furnace. The mixture fell on a material which had already been partly decomposed and in this way the fresh charge did not come into direct contact with the cast iron muffle; so corrosion was prevented. The stirring device mixed then the content thoroughly and pushed it slowly to the periphery of the pan. After conversion into neutral sulphate the lid of funnel *p* was opened and the stirring device carried the material into a truck beneath. The stirring device had four arms *m* in the form of a cross with interchangeable blades of ceramic or alloy steel.

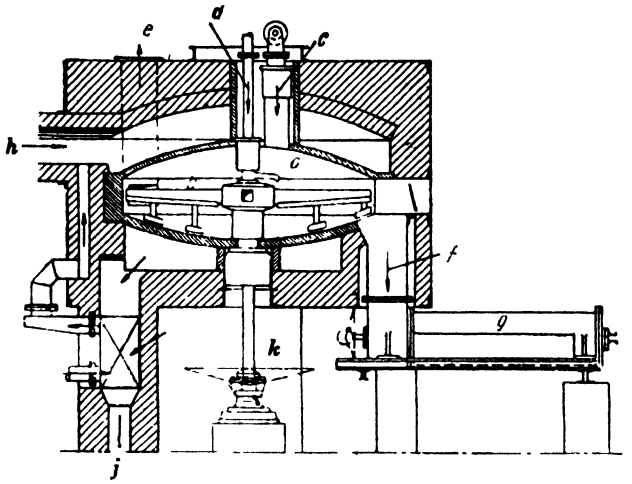


Fig. 111. Lurgi-Chemie mechanical furnace

a — muffle, *b* — arms of stirring device, *c* — salt feed into muffle, *d* — sulphuric acid inlet, *e* — hydrogen chloride outlet, *f* — sulphate discharge, *g* — rotating drum, water-cooled outside, *h* — inlet of producer gas, *j* — flue to stack, *k* — drive of stirrer.

The furnace was fired by gas evolved in a producer. First the cover of the muffle *g* was heated then the lower part. The flue gases were ultimately led into stack *s*. Temperature above the muffle reached about 900 °C while in the lower part 550 to 600 °C. The final sulphate left the furnace at 450 to 500 °C. The gases with a 30 per cent HCl content were led through pipe *k*, fitted at the side of the muffle, into a condensation equipment. The capacity of a muffle 3500 mm in diameter, with salt and bisulphate used as the raw materials, was equal to 7 000 kg of sulphate and 4 300 kg of hydrochloric acid 20/21 °Bé, per 24 hours.

Later on, the furnace was adapted for the use of sulphuric acid instead of bisulphate. In this case the acid was led in through the hollow shaft of the stirring device into the arms, and flowing out of these it was distributed over the salt.

The firm Lurgi-Chemie perfected the design of the Mannheim furnace (Fig. 111).

The cast iron muffle was replaced by a fireclay brick muffle. The arch was made of carborundum which conducted heat well and withstood the effect of sulphuric acid. The outer brickwork was circular in shape and not rectangular as in the Mannheim furnace. Consequently, the surface area of the muffle was smaller so that the loss of heat due to radiation was reduced to a minimum. The interchangeable blades on the four arms of the stirring device, which revolved at a velocity of 1 to 2 r. p. m., were made of carborundum which resists to wear and does not pollute the product either with iron or chromium. This is of great importance when manufacturing sulphate for glass works.

The shaft of the stirring device is cooled by water or air. The salt is brought to the furnace by a worm and the concentrated sulphuric acid (96 to 98 per cent) is brought from a measuring tank by a pipe leading through the muffle roof into a distributing vessel located at the central head of the stirring device. This has a tubular outlet, through which the acid is sprayed over the salt. The raw material reaches the centre of the furnace and is moved by the stirring arms towards the perimeter of the furnace. A reaction takes place which is followed by calcination of the formed sodium sulphate. This remains for 1 $^3/_4$ to 2 hours in the furnace. The hydrogen chloride is led in an upwards direction through a cast iron piping away from the furnace.

The furnace is fired by gas from the producer to 500—550 °C. The arch of the muffle is heated first and afterwards the flue gas enters the flues below the bottom. Before entering the stack the flue gases preheat the combustion air in a recuperator.

The sulphate discharged from the furnace falls into a horizontal drum with a stirrer and a water cooling jacket. Here the sulphate is cooled down to 60 °C. At the end of the cooling drum there is a screening device, consisting of a drum sieve which revolves together with the shaft of the stirrer. The fine part of the mixture is ground in a ball mill and filled into paper bags or wooden barrels, or loaded loose into railway trucks. The coarser part which amounts to some 5 per cent of the total output, is a mixture of undecomposed sodium bisulphate and sodium chloride. This mixture is ground in a disintegrator and either added to the salt charged into the furnace or sold as a low grade product.

If concentrated sulphuric acid containing 98 per cent H_2SO_4 is used and the muffle has 4500 mm in diameter, 13 — 15000 kg of sulphate and 20 — 23000 kg of a 30 per cent hydrochloric acid will be produced daily. Under proper operating conditions gases containing 40 to 60 per cent HCl can be obtained while the remainder consists of air which has penetrated into the muffle. The daily output of the furnace per 1 sq. m of the muffle, when 98 per cent sulphuric acid is used, amounts to some 500 kg of treated salt. If less concentrated acid is used the furnace output rapidly decreases. The quality of the sulphate produced depends on the temperature of the furnace; the higher the final temperature the less sodium chloride and acid sodium sulphate contained in the final product. However, a temperature exceeding 560 °C is not desirable as the construction

material of the furnace will deteriorate from thermal strain and iron chloride will be formed which will pollute the product.

Furnaces built by the firms Induschimie and Zieren are designed on the same principle as the Lurgi-Chemie furnace. On 1 sq. m. of their reaction bottom surface 650 to 750 kg of NaCl can be treated daily.

In the USA rotation furnaces built according to the Laury design (see Fig. 112) are frequently used. The basic feature is a horizontal rotating drum. At one end of the drum combustion chamber *A* is placed on a movable truck. The chamber is heated by oil. The drum is divided into two sections of different

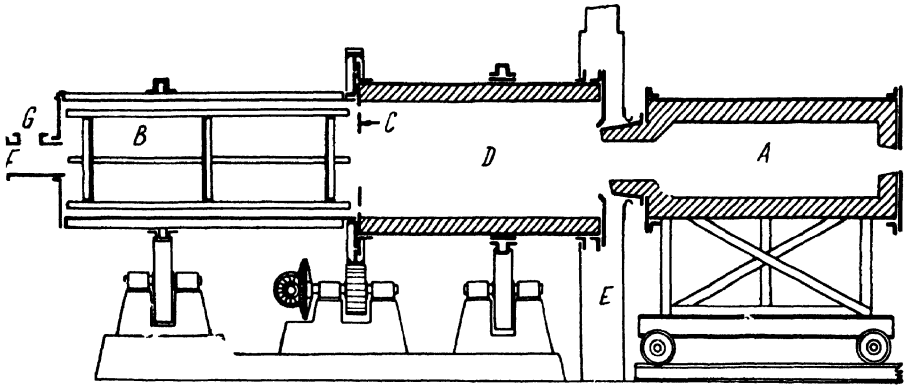


Fig. 112. Laury rotary sulphate furnace.

A — Oil heated movable chamber, *B* — first section of drum with cage made of steel bars, *C* — partition cast iron ring, *D* — second section of decomposing drum, *E* — sulphate discharge, *F* — hydrogen chloride and combustion gases outlet, *G* — raw material feed.

diameters. The raw material is fed through opening *G*. The section *B* which is lined with cast iron plates carries a steel bar cage. This scrapes the mass from the furnace walls and disintegrates it. In section *B*, the first stage of reaction is completed. The second section *D* of the drum is lined with fireproof bricks. The two sections are separated by a cast iron plate *C*, which has an opening in the center to allow the passage of gases and radial gaps close to the perimeter through which the crushed raw material passes from section *B* into section *D*, where the reaction is completed. From the furnace the product is continually discharged into chamber *E*. The hydrogen chloride released in the course of reaction and diluted by the products of the fuel combustion is drawn off through opening *F* in the axis of the drum and led to a dust separating chamber and therefrom into the absorption system. Although the gas obtained contains not more than 5 per cent HCl a standard concentration of hydrochloric acid can be manufactured from it in a suitable absorber.

Owing to more intense stirring of the reacting mass reaction takes less time

in a rotating furnace and capacity per unit of floor space is greater than in the case of mechanical furnaces. Also fuel consumption is almost by 50 p. c. less.

2. The manufacture of hydrogen chloride by the decomposition of sodium chloride with gases evolved during roasting of pyrites

In the Hargreaves-Robinson method sulphuric acid is avoided, and a hot mixture of sulphur dioxide, air and steam used instead.

Reaction occurs according to the following equation:

$$2\ NaCl + SO_2' + H_2O + 1/2\ O_2 = Na_2SO_4 + 2\ HCl;\ \Delta H^\circ_{291} = -50.7\ kcal, \quad (XII\text{-}4)$$

In order to make best use of the SO_2 the reaction gases are led into a system consisting of eight cylinders each 5.5 m high which are connected so as to form a battery (six of them operating, one being emptied and one being filled) and filled with sodium chloride briquettes. The gases first enter a cylinder filled with salt which is almost decomposed, then pass through further cylinders, and after passing through a cylinder filled with fresh salt briquettes they go to the absorption of hydrogen chloride. Gases containing 10 to 15 per cent HCl and 2 per cent SO_2 are obtained. Reaction temperature in the cylinders should be maintained at 500 °C. If the temperature falls below 400 °C, the reaction rate is negligible. Likewise reaction ceases at a temperature around 600 °C, when the salt melts.

Gases evolved during roasting pyrites containing some 8 per cent SO_2 on leaving the pyrite burners are utilized for the reaction. The gases are mixed with overheated steam and led into cylinders where they come into contact with salt briquettes stacked on a false bottom made of steel wire netting. The steel cylinders are provided with outside brickwork. Insulation of these cylinders must be very efficient to prevent excessive losses of heat released during the reaction. Hot flue gases pass through the annular space between the cylinders and the brickwork and heat the content of the cylinders to the reaction temperature, at the beginning of the process. The lids o cylinders are provided with openings through which the salt briquettes are charged. Hot and moist roasting gases are led to the cylinders (reactors) from a manifold and penetrate the salt from top to bottom. When the process starts the gases must be particularly hot and the salt preheated, so that the reaction attains the required velocity rate as quickly as possible.

Gases with a reduced content of sulphur dioxide and an increased content of hydrogen chloride are drawn off by a pipe which reaches to the false bottom, enter the cylinders and ultimately leave the last cylinder which is filled with a fresh charge of salt. The reaction gas is sucked off by a fan and passes to a hydrogen chloride absorption equipment. The final solid sulphate is discharged through an opening in the bottom of the furnace. The cylinders are 5.500 mm high and their output amounts to 55 000 kg of sulphate after 28 days

of operation. The Hargreaves method did not proved effective and was abandoned.

When hydrogen chloride is produced by the decomposition of common salt, sodium sulphate is the by-product. It contains 94 to 96 per cent Na_2SO_4, up to 2 per cent free sulphuric acid and up to 1.5 per cent NaCl. It is used specially in glass works but also in the manufacture of paper, dyes, sodium sulphide, ultramarine, Glauber's salt, cleaning powder etc. As sodium sulphate is of the utmost importance and more demanded than the hydrogen chloride sulphate, furnaces were often operated only for the purpose of production of this by-product. Today hydrogen chloride can be manufactured with better results on the basis of chlorine which is produced as a by-product in the alkali hydroxides manufacture. It is probable that the manufacture of sodium sulphate in sulphate furnaces will be less important in the near future as the artificial fibres industry offers a new, rich source of sulphate from waste spinbath liquors. By evaporation of such waste liquors Glauber's salt can be obtained. It can be marketed directly or dehydrated to anhydrous salt. In the USSR and the USA technicians have concentrated their efforts on the treatment of brines made from natural salts, available in these countries in the form of an anhydrous mineral thenardite and a dekahydrate called mirabillite. To a smaller extent, sulphate is also obtained in the form of Glauber's salt from waste liquors (which are the by-product in processing of the Stassfurt salts) as well as from the sea-water bitterns.

3. The manufacture of hydrogen chloride by direct reaction of chlorine with hydrogen

Hydrogen reacts with chlorine as follows:

$$H_2 + Cl_2 = 2\,HCl;\ \Delta\,H^{\circ}_{291} = -44.12\ \text{kcal} \qquad \text{(XII-5)}$$

The reaction yields a considerable amount of heat. At a lower temperature the reaction equilibrium is almost entirely shifted to the right side of the equation. Only when a temperature of 1700 °C is reached a certain quantity of free hydrogen and chlorine can be traced in the gas. When the stoichiometric mixture has been burnt, the theoretical temperature of the flame should equal 2400 °C. It will be lower if one gas is used excessively.

At a normal temperature and in darkness the rate of the synthesis of the gases will be a very low one. If the mixture should be heated or exposed to light, the reaction rate will rapidly increase and finally the reaction will acquire an explosive character.

The reaction of hydrogen and chlorine is one of the so called chain reactions. We may assume that the combining of every two molecules is followed by a whole chain of reactions innumerably reproduced. At a normal temperature and under low pressures this chain reaction is started and kept going by chlorine or hydrogen atoms; reactions of this type are described as mass chains.

A free atom of chlorine is formed when a chlorine molecule absorbs a quantum of light energy $\varepsilon = h\nu$:

$$Cl_2 + h\nu = 2\ Cl. \qquad \text{(XII-6)}$$

The chlorine atom will then react with the molecular hydrogen and hydrogen chloride and atomic hydrogen will be formed capable of combining with a further molecule of chlorine etc.:

$$Cl + H_2 = HCl + H \qquad \text{(XII-7a)}$$

$$H + Cl_2 = HCl + Cl \text{ etc.} \qquad \text{(XII-7b)}$$

According to conditions under which these two reactions proceed they can be reproduced innumerably and an extremely small amount of atomic chlorine may give rise to the formation of a considerable amount of hydrogen chloride.

At higher temperatures and under higher pressure the reaction of hydrogen with chlorine acquires an explosive character resulting from the chain giving off branches. It is assumed that some of the chlorine molecules are activated thermally and iniciate the following reactions:

$$Cl_2 + \text{energy} = Cl_2^x \qquad \text{(XII-8a)}$$

$$Cl_2^x + H_2 = 2\ HCl^x \qquad \text{(XII-8b)}$$

$$2\ HCl^x + 2\ Cl_2 = 2\ HCl + 2\ Cl_2^x \text{ etc.} \qquad \text{(XII-8c)}$$

Such chains are known as energy chains and are caused by activated chlorine molecules Cl_2^x which carry an abnormally great amount of energy acquired by absorption of heat. According to the reaction mechanism given above each activated chlorine molecule Cl_2^x first combines with a hydrogen molecule to two activated hydrogen chloride molecules. These two activated hydrogen chloride molecules then react and activate two new chlorine molecules, thus causing the chain to branch off rapidly. The greater is the accumulation of the heat released in the reaction space, the greater is, consequently, the possibility of the chlorine molecules being activated and the chain reaction being started. To avoid the danger of explosion during the reaction of hydrogen with chlorine it is, therefore, imperative that the heat is drawn away from the combustion space. Completely dry gases will not react one with another. Any trace of humidity may accelerate the reaction to such an extent that an explosion may occur.

Sometimes the reaction continues until all the available chlorine has been consumed. With mass chains the reaction ceases when two chlorine atoms or two hydrogen atoms collide and form a molecule. With energetic chains, activated molecules are deactivated when colliding with the walls of the vessel or with an inert gas molecule. Increased reaction surface obtained e. g. by the presence of splinters, or an admixture of indifferent gas will reduce the reaction rate.

For industrial purposes different designs of furnaces are used for combustion of chlorine in hydrogen. An essential feature of all these furnaces is the Bunsen quartz burner (see Fig. 113) which consists of two quartz pipes. A narrower one being inserted into a wider one and both covered in a steel casing.

Hydrogen is led into the burner through the outer pipe and the chlorine through the inner pipe. The top of the chlorine pipe is blinded. Its walls have usually slanting openings which cause the gases to whirl and so mix thoroughly. A small excess of hydrogen (from 5 to 10 per cent) is introduced into the reaction so that the acid produced will not contain unreacted chlorine. The volume of these two gases is measured by a diaphragm and differential manometer. The gases are led into the lower part of the furnace through water seals and controlling valves. The hydrogen chloride produced leaves at the top of the furnace for cooling and absorption.

When the furnace is put into operation the quartz stopper with mica slab is removed from the peep hole and carbon dioxide or nitrogen is led in through an auxiliary tube until the air has been expelled from the burner and the furnace. An auxiliary steel burner with burning hydrogen is then placed in which ignites the hydrogen in the main burner after the controlling valve has been opened. When the furnace has been heated to a certain degree the auxiliary burner is removed and chlorine is gradually introduced. When chlorine combines with the hydrogen the flame becomes bluish green. The air inlet is then shut off by the stopper and the amount of chlorine and hydrogen increased to the full capacity of the furnace.

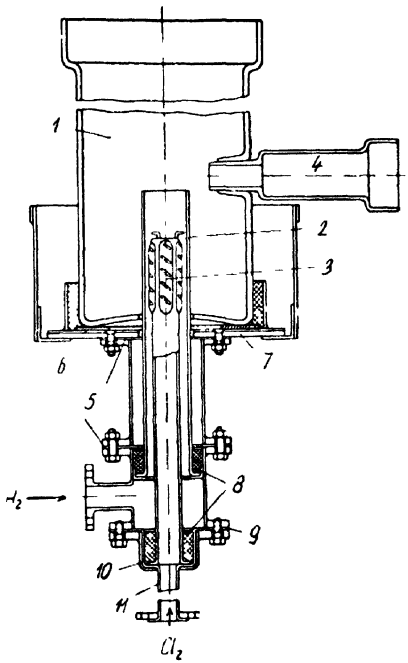


Fig. 113. Quartz burner for the combustion of hydrogen with chlorine.

1 — quartz combustion chamber, *2* — outer pipe of burner, *3* — inner pipe of burner, *4* — peep hole, *5* — packing, *6* — asbestos plate, *7* — supporting steel plate, *8* — putty, *9* — lead, *10* — steel, *11* — lead pipe.

In the course of the operation the pressure of both gases in the pipes must be closely observed. Should the pressure suddenly drop automatic valves will shut off the hydrogen and chlorine inlets and automatically introduce inert gas into the whole system. Leaving gases are subjected to a chlorine test with an aqueous solution of methylorange. Any decoloration of the methylorange is a sign of the presence of excessive chlorine so that the amount of chlorine introduced into the furnace must be reduced. For a normal interruption of the

operation the chlorine and hydrogen feeds are shut off and the lower part of the furnace is blasted with carbon dioxide.

The furnace itself is made of quartz, steel or lead. Formerly it was sometimes packed with contact material (fireproof bricks, fragments of quartz, lumps of graphite etc.). At present are furnaces built generally without packing.

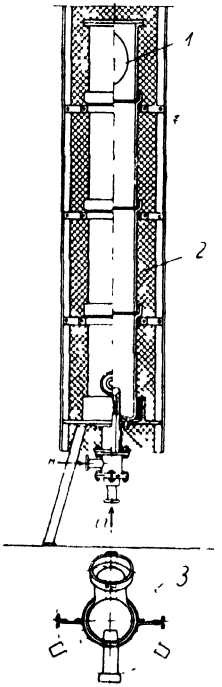


Fig. 114. Quartz furnace for hydrogen and chlorine combustion.
1 — hydrogen chloride outlet, *2* — wire grid, *3* — wire grid.

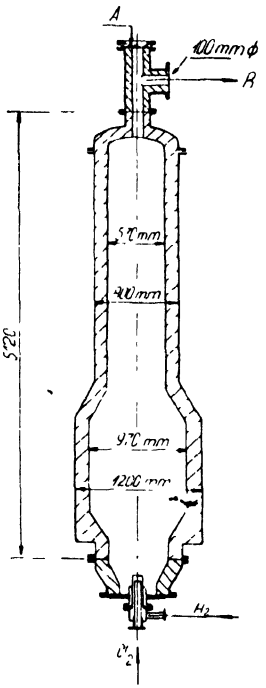


Fig. 115. Steel jacket furnace for the combustion of hydrogen and chlorine.
A — safety membrane, *B* — gaseous hydrogen chloride.

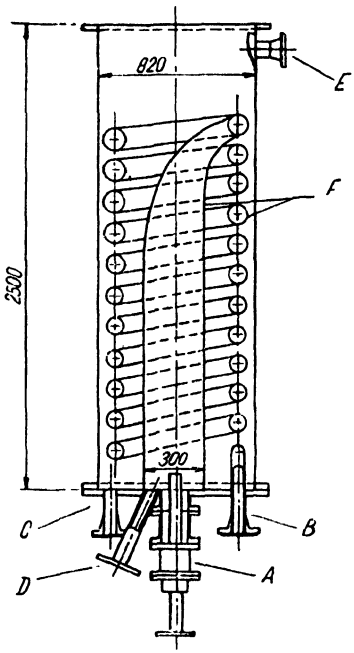


Fig. 116. Lead jacket furnace for the combustion of hydrogen and chlorine.
A — Quartz burner, *B* — hydrogen chloride outlet, *C* — water outlet, *D* — ignition and inspection window, *E* — cooling water inlet, *F* — lead central pipe and coil.

a) *Quartz furnaces*

The burner of a fused-quartz furnace (see Fig. 114) is placed at the bottom of a number of superimposed quartz sections in the form of pipe 1000 mm high and 400 mm in diameter. Into the lower section a pipe closed with a mica plate is inserted through which the hydrogen is ignited and the course of the process is inspected according to the colour of the flame. The lower part of the furnace is covered by a cylindrical steel jacket and rests on supports. The quartz sections

are covered completely by steel wire net which protects the operator in the event of an explosion.

b) *Steel jacket furnace*

A steel jacket furnace is shaped like a vertical tower (see Fig. 115) and is lined with acid resisting and refractory bricks. The overall length is 5120 mm, the outside diameter 800 mm at the top and 1200 mm at the bottom, inside diameter 570 mm at the top and 970 mm at the bottom. 3 600 kg of chlorine can be treated in furnaces of this type daily. Hydrogen and chlorine are brought to the valves by overpressure of 1 atm. and an overpressure of 0.5 atm. is maintained in the combustion chamber. The gas is drawn off through a side pipe which is 100 mm wide and fixed at the top of the furnace. A small safety membrane is also fitted at the top for the case of explosion.

c) *Lead jacket furnace*

A special type of a lead jacket furnace is shown in Fig. 116. In its lower part is placed a quartz burner which runs into a lead pipe, 300 mm in diameter and 2000 mm high, which tapers at the upper end. The pipe passes into a tube which winds in the form of a coil down the outside of the wider pipe. This coil serves as outlet of the hydrogen chloride. The whole is submerged in water in a vessel 820 mm in diameter and 2.500 mm high. The wider pipe can be also made of lead-coated steel and the coil can be made of a steel pipe covered with a protective varnish. The water bath which is cooled by water passing through it is maintained at a temperature of about 90 °C, so that the temperature of the gases is always kept above the dew point of the hydrochloric acid to prevent corrosion of the apparatus. The hydrogen chloride which leaves the combustion chamber at 700 °C passes through the cooling coil and is gradually cooled to a temperature of 100 °C at the end of the coil. In a furnace of the above given dimensions 3000 kg of chlorine can be treated daily.

4. The manufacture of hydrogen chloride from chloride and lighting or generator gas

Instead of pure hydrogen it is also possible to use lighting gas containing approx. 60 per cent H_2, 22 per cent CH_4 and 15 per cent CO. This is mixed with steam before being introduced into the burner. Approximately twice as much steam is used as theoretically required in proportion to the hydrocarbons and carbon monoxide present in lighting gas:

$$CH_4 + 2\ H_2O = CO_2 + 4\ H_2 \qquad \text{(XII-9)}$$

$$CO + H_2O = CO_2 + H_2. \qquad \text{(XII-10)}$$

The ratio of hydrogen to chlorine is adjusted so that after combustion an excess of about 10 per cent hydrogen is left in the final gas.

Generally, the steel jacket combustion furnace described above is employed

for the reaction. The mixture burns at a temperature of 800 to 900 °C and the gas leaving the furnace contains some 80 per cent HCl (expressed in terms of dry gas), at a temperature of some 600 °C.

It has also been proposed that hydrogen chloride should be manufactured by introducing steam and chlorine into a generator filled with glowing coke. The reaction which would then occur is expressed by the following equation:

$$C + 2\,H_2O_{(g)} + 2\,Cl_2 = 4\,HCl + CO_2;\ \Delta H^\circ_{291} = -66.7\ \text{kcal.} \quad \text{(XII-11)}$$

This reaction is sufficiently exothermic for the reaction temperature to be autothermically maintained at about 500 to 600 °C. However, the acid produced contains a considerable proportion of coke ash impurities.

5. By-product hydrogen chloride

Hydrogen chloride is a by-product of numerous organic chlorinations. The production of chlorobenzene is a typical instance:

$$H_6C_6 + Cl_2 = C_6H_5Cl + HCl, \quad \text{(XII-12)}$$

The gas leaving chlorination contains apart from hydrogen chloride small amounts of chlorine, benzene and chlorobenzene vapours. First of all the vapours of these organic substances are removed partly by condensation after being cooled in an externally water cooled coil and partly by absorption in cooled chlorobenzene in a small absorption tower. Hydrogen chloride is then absorbed in water. Hardly any chlorine contaminates the acid produced in the course of absorption as with a rising concentration of hydrochloric acid the solubility of the chlorine drops considerably. The remaining chlorine contained in the unabsorbed gases is ultimately absorbed in a tower scrubbed with milk of lime.

Similarly, hydrogen chloride also escapes during chlorination of other hydrocarbons as well as in the manufacture of monochloracetic acid, chloral, etc.

B. ABSORPTION OF HYDROGEN CHLORIDE IN WATER

1. Theoretical principles of absorption

A given amount of liquid can absorb gas only up to the concentration at which the partial pressure of the gas from the solution formed by absorption is equal to its partial pressure in the gas phase. If the partial pressure of the gas from the solution is lower than in the vapour phase, absorption sets in and the rate of absorption, at a given total absorption coefficient, depends on the difference in the partial pressures in the two phases and on the size of the contact surface. From the dependence of the partial pressures of hydrogen chloride on the composition of the hydrochloric acid it follows that the vapour pressure of HCl from diluted solutions is relatively very low. Therefore, practically all the hydrogen chloride from the gas phase can be absorbed, as

long as it is not necessary to produce concentrated solutions. On the other hand partial pressure of hydrogen chloride from more concentrated solutions is relatively high even at low temperatures. This means that for the absorption of hydrogen chloride proceeding under atmospheric pressure definite limits are set for the maximum concentration of the manufactured hydrochloric acid. In more concentrated solutions the partial pressure increases rapidly with a rising temperature; so in order to obtain concentrated hydrochloric acid the absorption must be carried out at as low a temperature as possible.

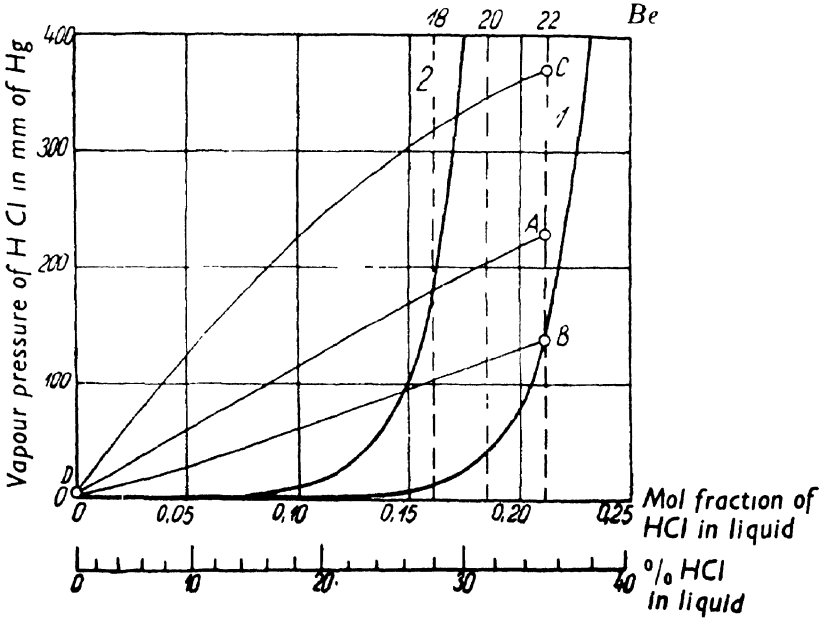


Fig. 117. Vapour pressures of HCl from hydrochloric acid.

Fig. 117 shows the dependence of equlibrium pressure of hydrogen chloride in mm of Hg on the hydrochloric acid concentration expressed in mol fractions, at 30 and 80 °C. (Curve *1* and *2*.).

Let us assume that at a temperature of 30°C a 35.2 weight per cent hydrochloric acid (to which a mol fraction $N_{HCl} = 0.21$ corresponds) is to be manufactured by the absorption from a gas containing 30 per cent HCl, which, at an overall pressure of 1 atm. has a partial pressure $p_{HCl} = 228$ mm Hg. In the diagram these concentrations are marked by point *A* which shows the conditions at the beginning of the absorption system where the manufactured acid meets the incoming gas. Let us assume further that the concentration of gases leaving the absorption system equals 0.3 per cent HCl ($p_{HCl} = 2.3$ mm Hg). The con-

centration of hydrochloric acid will be practically nil as at the end of the absorption system the gases meet almost pure water fed to the system. In the diagram this condition is expressed by the position of point *D*. If in a similar way we mark the points in the various sections of the absorption between the two final points of the absorption system we obtain curve *DA*.

As the equilibrium partial pressure of hydrogen chloride over a 35.2 per cent hydrochloric acid is only $p^{x}_{HCl} = 135$ mm Hg the gas under partial pressure $p_{HCl} = 228$ mm Hg will be readily absorbed in the acid (the difference in pressures $p_{HCl} - p^{x}_{HCl} = AB$ determines the absorption rate).

The line *CD* represents the absorption of gas containing 50 per cent HCl. From its position we can see that with this gas the difference $p_{HCl} - p^{x}_{HCl}$ in the whole of the absorption system is almost double of that one obtained with a 30 per cent gas so that absorption proceeds twice as fast, or at the same rate only half the contact surface between the gas and the liquid will be sufficient to obtain the same result as in the first instance.

Curve *2* represents the partial pressure of hydrogen chloride over the hydrochloric acid at 80 °C. It can be seen that this curve does not intersect the ordinate of the 35.2% hydrochloric acid. This means that from a gas with partial pressures of hydrogen chloride comprised in the diagram an acid of the required concentration cannot be produced.

A gas being in equilibirum with 28.5 per cent hydrochloric acid has at 80 °C a partial pressure of hydrogen chloride 188 mm Hg. At 30 °C, however, the partial pressure of hydrogen chloride reaches only 9.9 mm Hg. With more concentrated acids the difference is even greater. Higher temperatures prevent, therefore, the production of more concentrated hydrochloric acid. On the other hand with weak acids with concentration below 18 per cent (i. e. with a mol fraction below $N_{HCl} = 0.1$) the difference in partial pressures of hydrogen chloride corresponding to the both above-mentioned temperatures is small. From this observation a conclusion can be drawn for the industrial practice, to keep the temperature as low as possible in the part of the absorbing system where strong acid is to be manufactured. Contrariwise the temperature is unimportant when the absorbing acid is diluted.

When hydrogen chloride is absorbed by water a great amount of heat is released which causes a rise in temperature in the absorbers. Hence, if an acid with a high concentration is to be produced, the gases must not only be cooled before entering the absorption equipment, but also care must be taken to cool the absorbing liquid during the operation.

2. Absorption systems

When hydrogen chloride produced in sulphate furnaces is used for the manufacture of hydrochloric acid, the gases after being cooled to about 60 °C in quartz pipes outwardly sprayed with water are first led to stoneware towers packed with ceramic fillings or coke to remove the entrained mist of the sul-

phuric acid and the dust. A certain amount of polluted hydrochloric acid, containing 8 to 10 per cent H_2SO_4 leaves the towers. Usually it goes to the sewer. On the other hand the gas obtained from the reaction of hydrogen with chlorine is sufficiently pure; therefore, apart from cooling no other treatment is required prior to absorption.

The composition and the temperature of the gases introduced into the absorption process vary according to the type of furnace. From mechanical sulphate furnaces gas containing 40 to 60 per cent HCl escapes at 600 °C and Laury's rotary furnaces yield gas containing not more than 5 per cent HCl at 300 °C. The hydrogen chloride produced by burning hydrogen in a stream of high concentrated chlorine is very concentrated and when leaving the combustion furnace at a temperature of 700 to 800 °C it contains 90 to 95 per cent HCl.

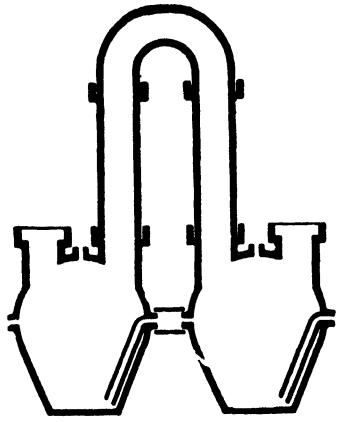


Fig. 118. Tourills for hydrogen chloride absorption.

If the gas is highly concentrated the rate of absorption by water is so high that it is unnecessary to use a complicated equipment to get the hydrogen chloride into intimate contact with the absorbent. On the contrary, it is imperative to lead the gas simply along to the water surface, so as to avoid a too intensive absorption and to prevent a sudden release of too great an amount of heat. As soon as the gas has been diluted and the value of the difference $p_{HCl} - p^{x}_{HCl}$ lowered, a tower packed with suitable stoneware fillings (Raschig rings, pots, slabs, balls, rhomboeders, dishes, spiral shapes etc.) or coke must be used to make the contact between the gas and the water as intimate as possible. At this stage no noticeable amount of heat is released and apart from this the rate of absorption no longer depends to such an extent on the temperature as it did in the first stage. Consequently, it is not necessary to maintain particularly low temperatures.

a) *Absorption in tourills or Cellarius absorbers*

Tourills or Cellarius absorbers were previously used for the absorption of hydrogen chloride. They were connected in series or in parallel into multiple batteries. In equipment of this type absorption was confined to the surface of the liquid.

Tourills are in principle Wolff's ceramic (stoneware) bottles, provided with two large connections at the top in which elbow pipes are fixed and sealed by a mixture of asbestos and water glass. The pipes serve for inlet and outlet of the gases (see Fig. 118).

Two additional small connections closed with rubber stoppers are fitted at the sides into which bent glass pipes are led. Through these flows the water or the weak acid for absorption. Absorption was carried out countercurrently. The weak acid leaving the absorption tower at the end of the battery entered the last tourill and flowed against the gas stream until it reached the first tourill and left it as concentrated acid. The concentrated gas, therefore, met already saturated hydrochloric acid. The residue of hydrogen chloride in the gas was absorbed in an absorption tower at the end of the absorption system of tourills. This tower was scrubbed with pure water and unabsorbed gases were led into the stack. The acid manufactured contains 32 to 35 per cent HCl and leaves the first tourill at a temperature of 40 to 60 °C to be cooled down to 20 °C in a stoneware coil immerged in a container filled with water. The drawback was here the extensive floor space, which was necessary, as the absorption heat was dissipated into the ambient atmosphere by natural heat radiation only. For this reason the system was only suitable for small and medium sized sulphate furnaces.

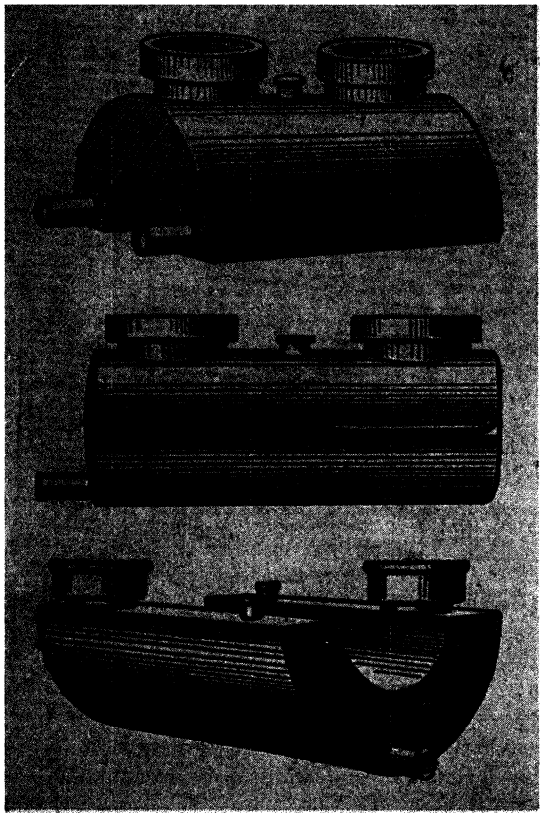


Fig. 119. Cellarius absorbers.

The *Cellarius* absorbers were known for their greater absorption capacity. The introduction of a special saddle shape of the absorbers made it possible to increase the cooling surface of the walls in proportion to the volume of the body. In order to increase the cooling effect the absorbers were placed in tubs through which water flowed. At the top of the absorbers there were two connections for the inlet and the outlet of the gas, and at the bottom connections were located to allow the passage of the absorption liquid (see Fig. 119).

b) *Absorption in quartzware absorbers*

From point of view of heat conductivity and resistance to changes of temperature thin fused quartz is a more suitable material than stoneware. The long S-bends are made of this material and piled into a high column. Usually S-bends are about 2000 mm long and 200 mm in diameter. They are connected together by asbestos and a suitable cement. As a rule two columns are set up in series: the first column working as a gas cooler and the second as an absorber (see Fig. 120). The body of both the cooler and the absorber is sprayed on the outside by water. Water or weak acid are introduced into the absorber for the absorption of hydrogen chloride. Gases leaving the combustion furnace at a temperature of about 800 °C are first cooled to a temperature of some 200 °C in a long quartz pipe. In a quartz cooler the temperature drops to about 60 °C. Gases enter the absorber at the bottom and flow countercurrently to the water flowing down from the upper part of the system. The bottom of the S-bend absorbers is flattened and its lower end has a shallow ridge which retains a certain amount of the liquid in the horizontal section of the pipe. This makes the S-bend absorbers to function like a set of superimposed tourills (see Fig. 121). Between individual S-bend absorbers at the upper end of the absorption battery are small towers, filled with quartz fragments or Raschig rings to improve absorption. The acid produced leaves the absorption station at a temperature of

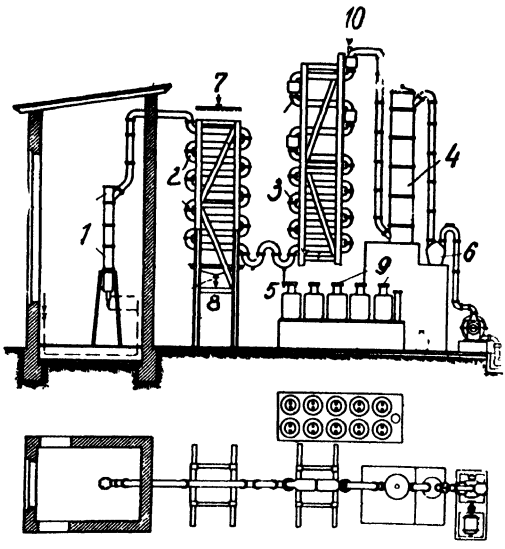


Fig. 120. Quartz absorption equipment for the manufacture of hydrochloric acid.

1 — Combustion furnace, *2* — Cooler, *3* — Absorber, *4* — Scrubber, *5* — Acid outlet, *6* — Tourill, *7* — Cooling water inlet, *8* — Cooling water outlet, *9* — Receivers, *10* — Water feed to the absorption column.

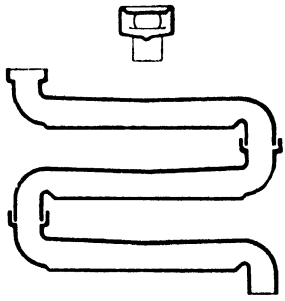


Fig. 121. S-bend absorbers for the hydrogen chloride.

45—60 °C, according to the season, its concentration being approximately 32 per cent HCl.

The body of both the cooling and the absorbing equipment are suspended in a steel or concrete structure out of doors. A part of the cooling water which flows down the surface of the pipes ventilated by ambient air evaporates which has an additional cooling effect. After the gas had passed through the absorber

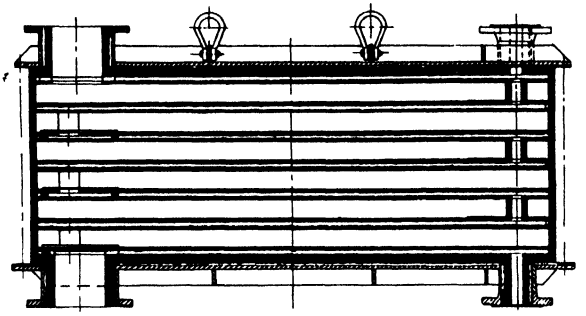


Fig. 122. Hydrogen chloride cooler made of igurite.

it is sometimes sucked off by means of a fan and passes then into an absorption tower located at the end of the absorption system. The weak acid which leaves this tower is introduced as an absorption liquid into the quartzware absorbers.

c) *Carbate or igurite coolers and absorbers*

Coolers and absorbers made of special graphite impregnated with synthetic wax (carbate, igurite) are very efficient for cooling and absorbing hydrogen chloride in water. Their construction is shown in Figs. 122 and 123.

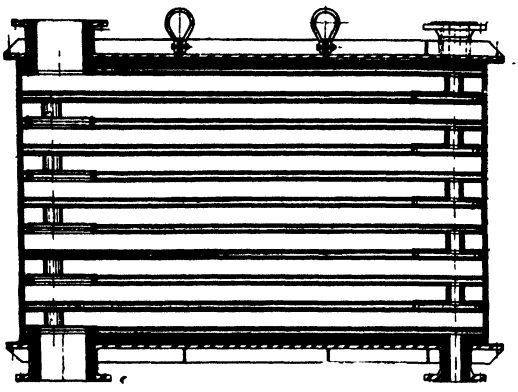


Fig. 123. Hydrogen chloride absorber made of igurite.

This cooler consists of a case made of graphite slabs. It is divided into six horizontal superimposed chambers, mutually connected by overflows. Gas enters the cooler from the bottom and passing through the chambers leaves at the top. In between the chambers are narrow clearances through which water flows in a downward direction and cools the hydrogen chloride flowing in an opposite direction. Small amounts of hydrochloric

acid which are condensed from the gases, are drawn off from the chambers through a liquid seal.

Hydrogen chloride vapour which after passing through the cooler has temperature of 30 °C, is led into an igurite absorber of a design similar to that of the cooler. This consists of ten chambers. The absorption water entering the chamber at the top, comes into direct contact with the gas flowing from the bottom. The cooling water from below enters the narrow spaces between the chambers.

The daily output of a cooler measuring 1650 × 610 × 350 mm and an absorber measuring 1650 × 970 × 350 mm equals 7.5 tons of 30 to 35 per cent hydrochloric acid. As a rule, two graphite absorbers are connected in series and the more diluted acid from the second absorber which contains about 20 per cent HCl is pumped into the first absorber. The rest of the unabsorbed gas is led through a rubber lined steel absorption tower into the atmosphere. The tower is sprayed with water and the diluted acid obtained is employed as an absorption liquid in the second igurite absorber. The flow of the tail gases is aided by a steam-jet ejector.

d) *Glass absorbers*

For the absorption of pure hydrochloric acid a system of long glass tubes is sometimes used. The tubes consist of three sections with an overall length of 6000 mm and diameter of 40 mm which are cooled outside by water flowing through the jacket. As here the absorption reaches but 75 per cent so must the remaining hydrogen chloride be absorbed in a tower.

e) *Tantalum absorbers*

The most efficient absorber for concentrated gases is an apparatus in which the main absorption process takes place in a double jacketed tower; the inner walls of the jacket are made of corrugated tantalum sheets resistant to hydrochloric acid. Gaseous hydrogen chloride together with weak hydrochloric acid, obtained in the second stage of absorption, enters the tower and passes through it from top to bottom. Cooling water flows between the two jackets in an opposite direction. The finished hydrochloric acid is collected in a special stoneware container, whilst unabsorbed gases leave through a stoneware piping for the second absorption stage. Here the gas enters the bottom of a stoneware tower packed with Raschig rings, passes through the packing, which is scrubbed with water. At this stage the absorption heat is drawn off by a tantalum tube cooler in the middle of the tower. The diluted acid then flows to the first tower, where after further absorption of hydrogen chloride it will yield concentrated acid containing up to 40 per cent HCl. After a final cooling in a glass cooler, the acid is led to storage tanks.

f) *Absorption of diluted gases*

Diluted hydrogen chloride vapour such as escape e. g. from Laury's sulphate furnace (5 per cent HCl) cannot be absorbed in any absorber with a cooled

surface. Therefore, a system of stoneware towers is used which are connected in series and filled with lumps of coke or Raschig rings. Pure water is led to the last tower and the weak acid formed is recirculated several times in the same tower and then pumped by stoneware or carbate pumps to the next tower in the opposite direction to the flow of the gases. When passing from one tower to another the diluted hydrochloric acid is usually cooled in a stoneware or carbate (igurite) cooler. A concentrated acid containing about 30 per cent HCl leaves the first tower. This concentration can be attained even with strongly diluted gas. The gas from the last tower which contains only traces of hydrogen chloride is drawn off to the stack.

C. LIQUID HYDROGEN CHLORIDE

Liquid hydrogen chloride is prepared from a gas obtained by burning a mixture of dry hydrogen and dry chlorine containing some 94 per cent HCl. The gas is first cooled in a quartz or igurite cooler and a small amount of condensed diluted hydrochloric acid is removed in the residue separator. Moisture is removed from the gas in a tower by scrubbing with concentrated sulphuric acid; finally, the dry gas is compressed to 1 atm. g. in one stage compressor and then once again to 15 atm. g. in a four stage compressor. The compressed gas is led through a layer of active carbon, in order to remove the phosgene (which was formed by the reaction of hydrogen chloride with the oil used for lubricating the compressors) and is finally liquefied in a brine-cooled condenser. It is shipped in steel cylinders.

D. USES OF HYDROCHLORIC ACID

Hydrochloric acid is stored in rubber lined steel storage tanks and shipped in rubber lined tank cars, pot cars or glass carboys. The following commercial grades of hydrochloric acid are known: synthetic hydrochloric acid which is prepared by the reaction of hydrogen with chlorine; sulphate acid obtained as a by-product in the manufacture of sodium sulphate; hydrochloric acid used in the foodstuff industry and finally chemically pure hydrochloric acid.

Contrary to the technical synthetic acid the characteristic feature of the sulphate hydrochloric acid is a higher sulphate content. The content of impurities in synthetic hydrochloric acid depends chiefly on the degree of purity of the absorption water. For the manufacture of pure acids distilled water is used and cooling as well as the absorption of hydrogen chloride vapours takes place in a quartz equipment. Similarly, the hydrogen leaving the mercury cells is first of all thoroughly freed of all mercury.

Technical hydrochloric acid is used in chemical industries especially for the preparation of inorganic salts and certain organic products, in hydrometallurgy, for washing sand, cleaning of metal objects, for etching and pickling of sheet iron, for the manufacture of glue, for dyeing of textiles etc.

Table 17. In Czechoslovakia, the following Standards are valid for hydrochlorid acid

	Muriatic acid			Hydrochloric acid		
	synthetic	Sulphate		Purissimum	Purum	Depuratum
	%	grade „H“ %	grade „S“ %	chemically pure %	p. s. (for analysis) %	pure %
H Cl min.	31	31	31	—	—	—
Cl_2 max.	0,01	—	—	0,0002	0,0002	0,0008
Fe max.	0,015	0,005	0,02	0,00005	0,0001	0,0005
SO_4 max.	0,005	1,5	1,5	0,0002	0,0002	0,0008
Residue from evaporation and calcination	0,03	—	—	0,0005	0,0005	0,005
As max.	—	0,002	0,005	0,000005	0,00001	0,00002
Heavy metals max.	—	—	—	0,0002	0,0003	0,001
SO_3 max.		—	—	0,0006	0,001	0,001

For certain purposes, such as for the production of vinylchloride which is intermediate for the production of polyvinylchloride plastics, for the manufacture of ethylchloride, ethylene chlorohydrin etc. the highest quality of gaseous hydrogen chloride is required. For its manufacture pure chlorine is used which is obtained by the evaporation of liquid chlorine, which is burnt with only a slight excess of hydrogen; the gas so obtained is dried in a tower by concentrated sulphuric acid and finally filtered through a layer of quartz or through polyvinylchloride bags. The hydrogen chloride so obtained then contains roughly 95 per cent HCl and 5 per cent $N_2 + H_2$.

XIII. SODIUM HYPOCHLORITE

Sodium hypochlorite belongs to the group of bleaching agents which contain available chlorine (e. g. bleaching powder, calcium hypochlorite and sodium chlorite). The bleaching effect of these compounds, which are used for the treatment of all kinds of vegetable fibres, is based on the oxidizing properties of the so called "active chlorine" the content of which is the distinctive characteristic feature of individual agents.

The term "active chlorine" means the amount of chlorine the oxidation power of which corresponds to that of the amount of gaseous chlorine liberated from a particular bleaching agent when reacting with hydrochloric acid. The content of active chlorine is expressed in per cents by weight in the case of solid substances or as a concentration (grams per litre) in the case of solutions. For instance 1 kg of bleaching powder containing 35 per cent active chlorine will normally yield 350 grams of chlorine, i. e. 109 litres when reacted with hydrochloric acid.

The relation between the oxidation power of gaseous chlorine and that of bleaching agents will be found in equations of their respective reduction processes when related to an equal number of electrons consumed. The reduction of chlorine proceeds according to the equation

$$Cl_2 + 2e = 2\ Cl^-,$$

while the reduction of chlorite, hypochlorite and chlorine dioxide with the same number of electrons consumed can be expressed as follows:

$$ClO^- + 2\ H^+ + 2e = Cl^- + H_2O$$
$$1/2\ ClO_2^- + 2\ H^+ + 2e = 1/2\ Cl^- + H_2O$$
$$2/5\ ClO_2 + 8/5\ H^+ + 2e = 2/5\ Cl^- + 4/5\ H_2O,$$

From these equations it is evident that 1 mole of chlorine has the same oxidation power as one gram-ion of ClO^- (i. e. one mole of NaClO or half a mole of $Ca(ClO)_2$), half a mole of $NaClO_2$. or finally, two fifths of a mole of chlorine dioxide. For example, one gram-molecule of pure calcium hypochlorite of 142.99 grams in weight has the same bleaching power as two moles of chlorine weighing 141.84 g. The content of active chlorine in this substance thus equals 141.84/142.99 = 99.19 per cent.

Sodium hypochlorite is a white hygroscopic substance the probable composition of which corresponds to the formula $NaOCl \cdot 6\ H_2O$. This compound is very unstable and decomposes easily under liberation of oxygen; due to this fact the preparation of crystaline salt is very expensive, so for technical purposes it is produced only as an aqueous solution. This can be done either by electrolysis or chemically by gaseous chlorine being introduced into a solution of sodium

hydroxide. The bulk of bleaching liquors is produced today exclusively by the second method, while the electrolytic method is used when bleaching liquors are required for immediate use on the spot, in small quanties.

A. ELECTROCHEMICAL PREPARATION OF HYPOCHLORITES

1. Theoretical principles

Aqueous solutions of alkali hypochlorites can be prepared under suitable operating conditions by the electrolysis of alkali chlorides in an electrolyzer without a diaphragm.

a) *Processes at the cathode*

When electrolyzing an aqueous solution of alkali chloride, hydrogen ions formed by the dissociation of water are discharged at the cathode:

$$2\ H_2O + 2e = 2\ OH^- + H_2 \qquad \text{(XIII-1)}$$

while hydroxyl ions are left in the solution, whereby the electrolyte acquires an alkaline reaction Platinum or graphite is used as the cathode material.

Apart from this main reaction, there may occur a reduction of hypochlorite ions at the cathode:

$$ClO^- + 2\ H^+ + 2e = Cl^- + H_2O. \qquad \text{(XIII-2)}$$

In this reaction, which is responsible for the losses of active chlorine and a lowering of current efficiency, the hypochlorite acts as a depolarizer of the hydrogen evolution.

An access of ClO^- ions to the cathode is substantially hindered by the addition of a small amount of alkali chromate in the electrolyte. The presence of this compound lowers the loss of hypochlorite (due to the reduction of the latter) from some 30 per cent to 0.5—1 per cent. This favourable effect of the chromate is ascribed to its reduction at the cathode and formation of insoluble lower oxides CrO(OH), or $Cr(OH)CrO_4$ which envelop the entire cathode in form of a film:

$$CrO_4^{--} + 5\ H^+ + 3e = CrO(OH) + 2\ H_2O. \qquad \text{(XIII-3)}$$

This thin film prevents the access of ClO^- ions to the cathode but allows the liberated hydrogen to escape into the atmosphere and, also, the hydroxyl ions to migrate from the cathode into the bulk of the electrolyte. Chromate can be used only in a neutral or a slightly acid solution because the protecting film dissolves in strongly acid as well as in strongly alkaline solutions.

Chromate cannot be added to bleaching liquors used for the treatment of textiles, as it stains them and can be removed only with great difficulty. In this case the cathodic reduction of hypochlorite can be partially suppressed by the addition of calcium chloride together with high molecular aliphatic compounds

of sulphur (e. g. Turkey red oil), or with salts of sulphonated fatty acids or resin soaps. Calcium salt will be precipitated in the alkaline catholyte together with the organic substance under formation of an insoluble film which sticks to the electrode.

b) *Processes at the anode*

Chloride ions are discharged at the anode preferentially due to the high oxygen overvoltage

$$2\,Cl^- = Cl_2 + 2e. \qquad \text{(XIII-4)}$$

According to Faraday's law both anodic and cathodic products, i. e. hydrogen, sodium hydroxide and chlorine are formed in equivalent quantities. As there is

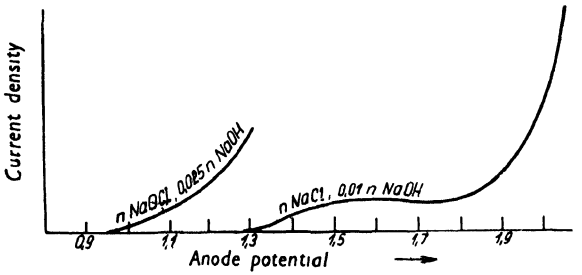


Fig. 121. The interdependence of the anode potential and current density during the electrolysis of a normal solution of sodium hypochlorite and of a normal solution of sodium chloride on smooth platinum electrodes.

no diaphragm to separate the catholyte from the anolyte, both the hydroxyl ions and the chlorine which is dissolved in the brine move countercurrently from the electrodes into the bulk of the electrolyte where they meet and react according to the following equation:

$$Cl_2 + 2\,OH^- = Cl^- + ClO^- + H_2O. \qquad \text{(XIII-5)}$$

The hypochlorite ions ClO^- thus formed may accumulate in the electrolyte up to a certain degree. When a higher concentration is attained, hypochlorite ions migrate and diffuse toward the anode and are discharged according to the equation:

$$6\,ClO^- + 6\,OH^- = 2\,ClO_3^- + 4\,Cl^- + 3/2\,O_2 + 3\,H_2O + 6e. \qquad \text{(XIII-6)}$$

The easy oxidation of hypochlorite ions is seen in Fig. 124 which illustrates the dependence of current density upon the anode potential during the discharge of chloride ions in a slightly alkaline normal solution of sodium chloride (right curve) and during the discharge of hypochlorite ions in a slightly alkaline normal solution of sodium hypochlorite on smooth platinum.

It will be seen from the graphical representation that ClO^- ions are discharged at a much lower anode potential, i. e. in preference to Cl^- ions, if the concentration is the same for both kinds of ions. We can, therefore, conclude that in a concentrated chloride solution with a much lower hypochlorite content the oxidation of hypochlorite will occur simultaneously with the chlorine liberation at a potential necessary for the later process, as the current curve of the hypochlorite oxidation will be within the range of the discharge potentials of Cl^- ions even at very low concentrations of ClO^- ions.

It should be noted that in spite of the easy discharge of hypochlorite ions at the anode a solution with a fairly high hypochlorite content can be prepared electrochemically; this can be explained as follows. Chlorine liberated at the cathode and subsequently dissolved in the brine reacts with water to yield hydrochloric and hypochlorous acid according to equation (XI-12), or according to equation:

$$Cl_2 + OH^- = HOCl + Cl^-. \qquad \text{(XIII-7)}$$

Owing to a negligible dissociation of hypochlorous acid the concentration of hypochlorite ions is very minute so that their oxidation at this stage of the electrolysis does not occur practically.

After formation, the hypochlorous acid diffuses into the bulk of the electrolyte and only here finds a sufficient quantity of hydroxyl ions for the following reaction to take place:

$$HOCl + OH^- = ClO^- + H_2O. \qquad \text{(XIII-8)}$$

In this way hypochlorite ions are gradually accumulated in the electrolyte, and, after their concentration has reached a certain value, they begin to migrate together with the chloride ions toward the anode, where they start being oxidized according to equation (XIII-6).

Thereafter, the hypochlorite concentration in the bulk of the solution increases still more slowly as electrolysis proceeds. An increasing number of hypochlorite ions will migrate towards the anode and will be there discharged in preference to Cl^- ions, until the amount of ClO^- ions formed by the neutralization of hypochlorous acid is equal to the amount of ClO^- ions discharged. At this moment the hypochlorite concentration in the electrolyte is at a maximum and will not further increase. The electric current, if we disregard the small discharge of the hydroxyl ions, will be consumed exclusively for the formation of chlorate, the content of which will increase rapidly. This state, when all the hypochlorite formed in a unit of time is converted by anodic oxidation to chlorate, is expressed by the total of equations (XIII-4), (XIII-5) and (XIII-6).

$$6\,Cl^- + 12\,OH^- = 6\,ClO^- + 6\,H_2O + 12e \qquad \text{(XIII-9)}$$

(formation of hypochlorite)

$$6\,ClO^- + 6\,OH^- = 2\,ClO_3^- + 4\,Cl^- + 3\,H_2O + 3/2\,O_2 + 6e \qquad \text{(XIII-10)}$$

(oxidation of hypochlorite)

$$2\,Cl^- + 18\,OH^- = 2\,ClO_3^- + 9\,H_2O + 3.2\,O_2 + 18e \qquad \text{(XIII-11)}$$

It will be seen from the last equation that once a stationary state has been reached only 12 Faraday's charges out of 18 are used in the formation of chlorate, while the remaining six are wasted in deposition of 3 gram-atoms of oxygen, which freely escapes from the electrolyzer. From the moment when the concentration of hypochlorite attains a constant value, the yields of hypochlorite drop to zero and the yields of chlorate attain the upper limit of 66.67 per cent, supposing that no oxygen will be lost in any process apart from reaction

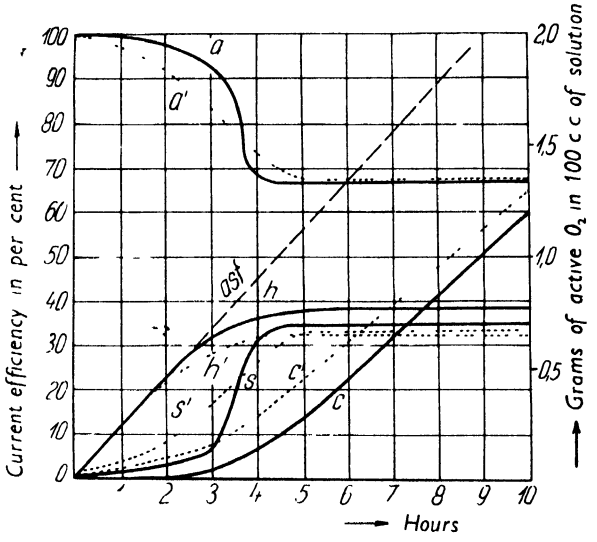


Fig. 125. Dependence of current efficiency upon time during electrolysis of a neutral solution of sodium chloride without the use of a diaphragm.

(XIII-6). This condition is arrived at if a concentrated neutral solution of alkali chloride is electrolyzed and reduction of hypochlorite at the cathode is prevented by the addition of alkali chromate.

Chlorate concentration increases during electrolysis, but exerts no influence upon the process, as its decomposition voltage is much higher than that of chloride. Chlorate ions are oxidized into perchlorate ions not sooner than the chloride concentration in the electrolyte drops below 5 % of the initial value. Therefore, chlorate can accumulate in the solution up to the saturation.

If we combine equations (XIII-11) and (XIII-1) we obtain a formula which characterizes the whole process of electrolysis of sodium chloride from the moment when the hypochlorite concentration attains a constant value and the whole current is consumed in forming chlorate and oxygen:

$$2\,Cl^- + 9\,H_2O = 2\,ClO_3^- + 9\,H_2 + 3/2\,O_2. \qquad \text{(XIII-12)}$$

This equation indicates that the whole solution remains neutral.

A clear picture of the course of electrolysis of sodium chloride solution with a concentration of 5.1 moles of NaCl per litre at 12 °C and a current density of 6.7 A/sq. cm can be seen in the graphical representation in Fig. 125.

The curves in full line are valid for electrolysis when platinized platinum anodes are used while the dashed lines show electrolysis effected with smooth platinum anodes. Curve *a* indicates the percentage of the whole current used for fixing oxygen in form of hypochlorite and chlorate while curve *s* represents the amount of current lost in the liberation of gaseous oxygen. If there is no loss of oxygen, the content of fixed oxygen should increase along the line *ast*, which has been calculated from the amount of electricity passing through the electrolyzer. Curve *h* indicates the change in concentration (in grams per 100 ml of electrolyte) during electrolysis of oxygen fixed in hypochlorite while curve *c* expresses the analogical change in chlorate oxygen concentration. At the beginning of electrolysis all current is consumed for the formation of chlorine which reacts quantitatively with the cathodic hydroxide to form hypochlorite so that current efficiency is 100 per cent as far as fixed oxygen is concerned. As electrolysis proceeds, the hypochlorite ions accumulated in the bulk of the electrolyte migrate in an increasing number towards the anode where they are instantaneously oxidized into chlorate with a simultaneous liberation of oxygen; this can be seen from the drop in curve *a* (down to 66.7 per cent) and the rise of curve *s* (up to 33.3 per cent). Finally, (roughly within 4 hours in this case) a point is reached when an equal number of hypochlorite ions is formed and discharged at the same time (see graph illustrating the change of curves *a* and *s* into horizontal lines). Simultaneously the amount of oxygen equivalent to the formed hypochlorite reaches a maximum and does not change any more (see the horizontal part of curve *h*), while curve *c* continues to rise, which proves that the chlorate concentration increases still further.

The discharge potential of chloride ions on smooth platinum at a given current density is some 0.6 V higher than on platinized platinum (it is still higher on magnetite); this causes that ClO^- ions commence to discharge at this electrode at a lower concentration, i. e. the liberation of oxygen and the formation of chlorate occurs sooner than on platinized platinum. For this reason curve *h'* which represents the course of the concentration of hypochlorite oxygen is always below curve *h* while curve *c'*, which is related to chlorate oxygen, is always above curve *c*.

If we study the graphical representation more carefully we see that the maximum current efficiency of 66.67 per cent in chlorate formation can only be obtained if a smooth platinum anode is used. An anode of platinized platinum (i. e. coated with platinum black) has a slightly lower efficiency as a certain amount of hydroxyl ions are discharged on the anode under liberation of oxygen due to the lower oxygen overvoltage at the anode material. (With graphite and magnetite anodes current efficiency is still lower.) Therefore, if the operation is performed in a neutral solution smooth platinum is the best material for the anodes, as far the production of chlorate is concerned. On the other hand,

bleaching liquors should be prepared with anodes of platinized platinum as with them the most concentrated solutions of hypochlorite can be obtained.

c) *Conditions for the production of hypochlorite*

It follows from the above explanation that electrolysis of alkali chlorides in an electrolyzer without a diaphragm must be interrupted before curve *h* which represents the concentration of hypochlorite oxygen changes into a horizontal line; only under this condition is the process economical, as a prolonged electrolysis would result in a waste of current without any further increase in the hypochlorite content. Moreover, care should be taken to prevent the hypochlorite ions formed from being electrochemically oxidized, as this would result in lower current efficiency and lower hypochlorite concentration in the liquor produced. This process is influenced by a number of factors, e. g. brine concentration, hydrogen ion concentration, anode material, current density, temperature, and last but not least a suitable design of the electrolyzer.

α) *Influence of brine concentration*

At first sight, a high concentration of salt in the electrolyte might appear advantageous, as in such a solution Cl^- ions would participate in current conduction rather than ClO^-, so that the amount of hypochlorite ions migrating to the anode would be smaller. Apart from this, the chloride ions from a concentrated solution would be anodically discharged at a lower potential at which the part of current consumed for the simultaneous oxidation of hypochlorite ions would be smaller and thus the hypochlorite yield higher. With regard to the best utilization of the salt we arrive, however, to a different conclusion.

The higher the concentration of the solution, the higher the consumption of sodium chloride to produce 1 kg of hypochlorite. As the value of the salt which is not entirely utilized in the bleaching liquor (salt cannot be recuperated from the used solutions) outweighs the savings from better current efficiency, it is economically better to renounce the advantage of a high brine concentration. So in practice the brine concentration is chosen according to the required concentration of hypochlorite solution. A less concentrated brine is used to produce a less concentrated hypochlorite solution and vice versa.

β) *Influence of the hydrogen ion concentration*

As far as pH of the solution is concerned, best current efficiency is obtained with neutral electrolytes for the following reasons. If we add a small amount of hydrochloric acid to the electrolyte, hypochlorous acid will be set free from hypochlorite:

$$NaOCl + HCl = HOCl + NaCl, \qquad \text{(XIII-13)}$$

The hypochlorous acid will then react with the remaining hypochlorite to yield chlorate:

$$NaOCl + 2\ HOCl = NaClO_3 + 2\ HCl, \qquad \text{(XIII-14)}$$

whereby the hypochlorite concentration is lowered. In a strongly acid medium no hypochlorite at all is formed as no hydroxide is formed at the cathode; therefore all the chlorine liberated escapes in a gaseous form at the anode.

A similarly unfavourable influence upon hypochlorite production exerts the presence of a free base in the electrolyte. If platinized platinum is used as electrode (at which the discharge potential of hydroxyl ions in an alkaline medium is comparatively low), oxygen is liberated instead of chlorine and no hypochlorite is formed at all. Smooth platinum, however, has a high oxygen overvoltage which enables the preferential evolution of chlorine. In spite of this, the hypochlorite yield is low in this case, because the anodically liberated chlorine meets hydroxyl ions in abundance already in the close proximity to the electrode; thus the hypochlorite ions formed close to the anode are readily oxidized into chlorate soon after their formation (according to equation (XIII-6)). A still lower yield of hypochlorite is obtained, if the operation is carried out at a higher temperature; under such condition, hydroxyl ions discharge on platinum under the evolution of oxygen to a greater extent owing to a decrease in the oxygen overvoltage.

γ) Influence of the material of anodes

Only platinum and graphite are suitable materials for anodes. Magnetite does not sufficiently withstand high current densities, and furthermore the product becomes contaminated with iron. The best material available would be platinized platinum, as its chlorine overvoltage is by some 0.6 V lower than with smooth platinum (at higher current densities). Unfortunately platinizing does not last long. For this reason smooth platinum is used and its high chlorine overvoltage is compensated for by using high current densities which are advantageous to hypochlorite production as they assist the discharge of chlorine ions preferentially to hypochlorite ions; apart from this, oxygen overvoltage rises with current density more rapidly than chlorine overvoltage. Due to its high price platinum electrodes are not widely used in commercial installations.

Graphite anodes are much cheaper but do not stand up to very high current densities and desintegrate rapidly; moreover, after the chloride contained within the pores is depleted, the hypochlorite ions and also hydroxyl ions are discharged in a greater extent. Consequently, the vicinity of the electrode becomes more acid than in the case with a platinum electrode and the reaction (XIII-14) takes place with subsequent losses of hypochlorite. Therefore, graphite anodes are only satisfactory when weaker bleaching liquors are being produced.

δ) *Influence of current density*

It can be seen from the above explanation that hypochlorite is virtually an unstable product of electrolysis regarding its easy electrochemical oxidation to chlorate. One way of suppressing oxidation of the hypochlorite ions at the anode is to increase the current density on the electrode to such a high value so that the main part of the current will be consumed in producing chlorine, and

only a minor part in the discharge of ClO^- ions, as the diffusion rate of these ions towards the anode reaches its upper limit at higher current densities.

ε) *Influence of the cell design*

In a suitably designed cell, the undesirable anodic discharge of ClO^- ions can be effectively limited e. g. in such a way that hypochloric acid and hydroxide are allowed to react in sufficient distance from the anode. Thus the diffusion of hypochlorite ions towards the anode is almost completely prevented. A design of a cell of this kind is illustrated in Fig. 126.

Anode *A* is arranged in a hollow in the bottom of the electrolyzer tank so that the solution surrounding it is not carried away by the slow flow of brine through the vessel. Cathode *K* is arranged as near as possible above the anode. Chlorine evolved at the anode rises in the electrolyte and reacts with the alkali hydroxide dripping from the cathode; the hydrochlorite solution so formed flows slowly from the electrolyzer.

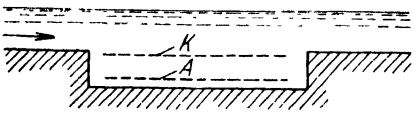


Fig. 126. Arrangement of electrodes in a Kellner electrolyzer: *A* — Anode, *K* — Cathode

In this way, a higher hypochlorite concentration can be attained than would be possible with an electrolyzer of normal design. An electrolyzer with electrodes arranged in an opposite way to that of Fig. 126 would make the situation rather worse, because hydrogen bubbles would rise from below and whirl the layer of the anolyte at the higher electrode, thus supporting the stirring of the electrolyte and an access of hydrochlorite ions towards the anode, the very thing we want to avoid.

ζ) *The effect of temperature*

Hypochlorous acid formed at the anode by hydrolysis of dissolved chlorine reacts with hypochlorite according to the equation (XIII-14). This undesirable process can be partially suppressed by maintaining a low temperature of the electrolyte. The cooling of the solution is still more important when higher current densities are used. A low temperature is, however, disadvantageous as far as energy consumption is concerned, as the ohmic resistance of the electrolyte increases.

d) *Energy consumption*

The main technical problem is to prepare sufficiently concentrated hypochlorite liquors (some 20 grams of active chlorine per litre) with an adequate consumption of electrical energy and common salt. The theoretical requirement for the preparation of 1 kg of active chlorine is 0.82 kg of NaCl, while the actual consumption is between 5 and 10 kgs.

For the deposition of 1 gram-equivalent of active chlorine 26.82 ampere-hours are needed; 1 kg of chlorine would thus require 757 ampere-hours according

to Faraday's law. The theoretical voltage necessary for the electrochemical decomposition of chloride under the formation of hypochlorite can be calculated from the known standard potentials which correspond to the processes at either electrode. The reduction potential at the cathode, where a reaction occurs according to (XIII-1), will be in a neutral medium ($a_{OH^-} = 10^{-7}$), at hydrogen pressure $p_{H_2} = 1$ atm., and at 25 °C as follows:

$$\pi_{OH^-|H_2,Pt} = \pi^{\circ}_{OH^-,H_2,Pt} - \frac{RT}{2F} \ln p_{H_2} a_{OH^-} =$$

$$= -0.828 - 0.05915 \log 10^{-7} = -0.414 \text{ V.} \qquad \text{(XIII-15)}$$

On calculating the anode potential we assume that hypochlorite is formed directly by the electrochemical oxidation of chloride according to the equation which results from equations (XIII-4) and (XIII-5):

$$Cl^- + 2\,OH^- = ClO^- + H_2O + 2e \qquad \text{(XIII-16)}$$

The standard oxidation potential related to this reaction at 25 °C is $\varepsilon^{\circ}_{Pt,|Cl^-,ClO^-} = -0.94$ V. The value of the potential in a neutral solution ($a_{OH^-} = 10^{-7}$) with unit activity of both chloride and hypochloride ions ($a_{Cl^-} = a_{ClO^-} = 1$) follows from the Nernst equation:

$$\varepsilon_{Pt|Cl^-,ClO^-} = \varepsilon^{\circ}_{Pt|Cl^-,ClO^-} - \frac{RT}{2F} \ln \frac{a_{ClO^-}}{a^2_{OH^-} a_{Cl^-}} =$$

$$= -0.94 + 0.05915 \log 10^{-7} = -1.354 \text{ V.} \qquad \text{(XIII-17)}$$

On adding the reduction and oxidation potential we obtain the value of the theoretical decomposition voltage at 25 °C:

$$(E_R)_t = -E'_{min} = -(\pi_{OH^-|H_2,Pt} + \varepsilon_{Pt|Cl^-,ClO^-}) = 1.768 \text{ V.} \qquad \text{(XIII-18)}$$

According to this result the minimum voltage required for the electrochemical production of hypochlorite equals 1.768 V. So, theoretically, for the preparation of 1 kg of active chlorine 1.338 kw-hr. are required. As a matter of fact, the energy required is much higher. This is mainly due to higher voltage caused by the high chlorine overvoltage at a high operating current density and by a rather high resistance of the electrolyte, the temperature of which is kept as low as possible. For this reason, the operating voltage across the electrolyzer is 4.0 to 6.5 V according to the electrodes used. The actual energy consumption when producing a liquor with 20 grams of active chlorine per one litre amounts to some 6 kw-hr. per 1 kg of active chlorine and the consumption of common salt is about 7 kg. With higher concentrations of active chlorine in the electrolyte the amount of energy increases rapidly, while the consumption of salt decreases, and vice versa.

On comparing the energy consumptions of an electrochemical production of hypochlorite liquor with the indirect method of producing hypochlorite from

chlorine and hydroxide, it will be seen that the second method requires only 3 kw-hr. for the preparation of 1 kg of active chlorine. For this reason the electrochemical preparation of hypochlorite bleaching liquors is only justified in very small plants where the cost of electrical energy compared with other costs is not important. In larger factories, however, the indirect method is exclusively used for the preparation of hydrochlorite.

2. Electrolyzer designs

Electrolyzers with platinum, graphite or combined electrodes which work intermittently or continuously are used for the production of sodium hypochlorite. The best results are obtained with platinum electrodes; these were widely used as long as the price of platinum was not so prohibitive as today.

a) *The Kellner electrolyzer*

The Kellner electrolyzer with platinum electrodes arranged horizontally is one of the most efficient cells. The electrolytic vessel has a cascade-like bottom which

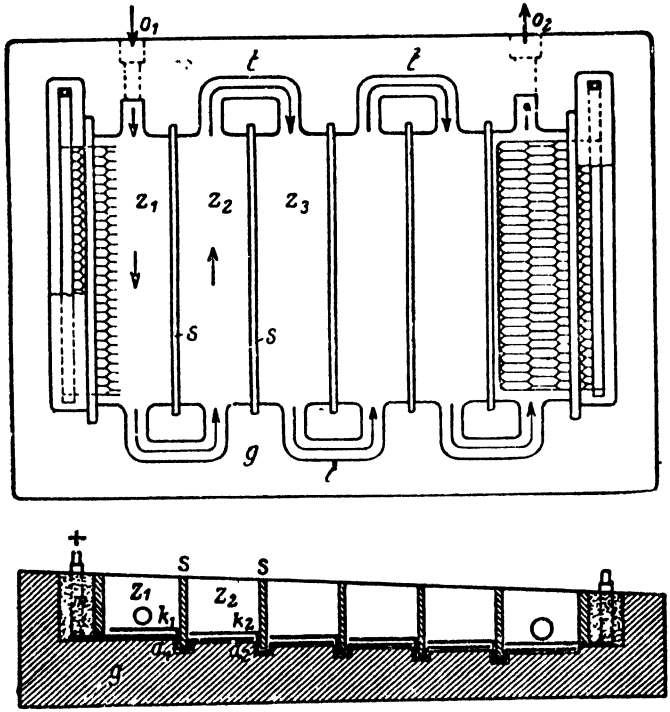


Fig. 127. The Kellner electrolyzer for production of hypochlorite liquor.
g — Electrolytic vessel, O_1 — Brine inlet, O_2 — Brine outlet, s — Glass partitions, l — Side channels, z_1, z_2, z_3 — Compartments, $k1$, k_2 — Cathodes, a_1, a_2 — Anodes.

is made of concrete or sandstone. Glass partitions s divide the vessel into a number of compartments z_1, z_2, z_3, which are interconnected by side channels. Platinum-irridium gauzes are used as bipolar electrodes. Half of the electrode rests on the bottom in a narrow hollow and acts as anode a, while the other half is situated some 5 mm higher above the bottom of the neighbouring compartment, situated slightly higher, and serves as cathode k. The electrodes pass below

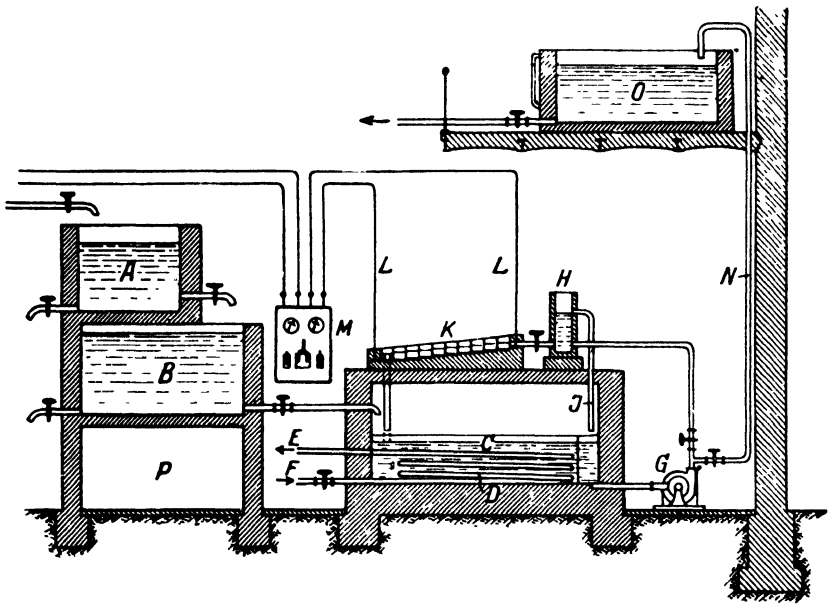


Fig. 128. Kellner plant for hypochlorite production

A — Brine purification tank, *B* — Decantation tank, *C* — Cooler of decanted brine, *D* — Cooling coil, *E*, *F* — Inlet and outlet of cooling water (coil D), *G* — Pump, *H* — Brine container, *J* — Overflow pipe, *K* — Electrolyzer, *L* — Current leads, *M* — Control panel, *N* — Piping for the finished liquor, *O* — Tank for finished product

the glass partitions, which fit firmly into the grooves. The first and the last compartment are provided with current leads, connecting the gauze electrodes to the source of current. The spacing of about 5 mm between anode and cathode in individual compartments is maintained by small glass rods (see Fig. 127).

The brine containing some 15 per cent of sodium chloride is admitted to the electrolyzer at o_1 and flows through the compartments which are arranged in cascades, and is let out at o_2. The warmed electrolyte is cooled in a suitable cooler, and recirculated until the required concentration of active chlorine is attained. An electrolyzer with 36 compartments takes 60 A at a total voltage of 220 V. The temperature of the brine is maintained at 21 °C. Calcium chloride and Turkey red oil are added to the brine to lower cathodic reduction.

The Kellner electrolyzer represents a very successful design as far as the electrochemical process is concerned. Because of the horizontal flow of the electrolyte a quiet diffusion layer is maintained at the anode; the anodes are placed close to the bottom of the electrolyzer, so as to assure the complete absorption of chlorine, while the cathodes are arranged so as to prevent the liberated hydrogen from stirring the electrolyte. Finally, the high current density makes it possible to attain high current efficiency, and to produce sufficiently concentrated bleaching liquors with a relatively low energy con-

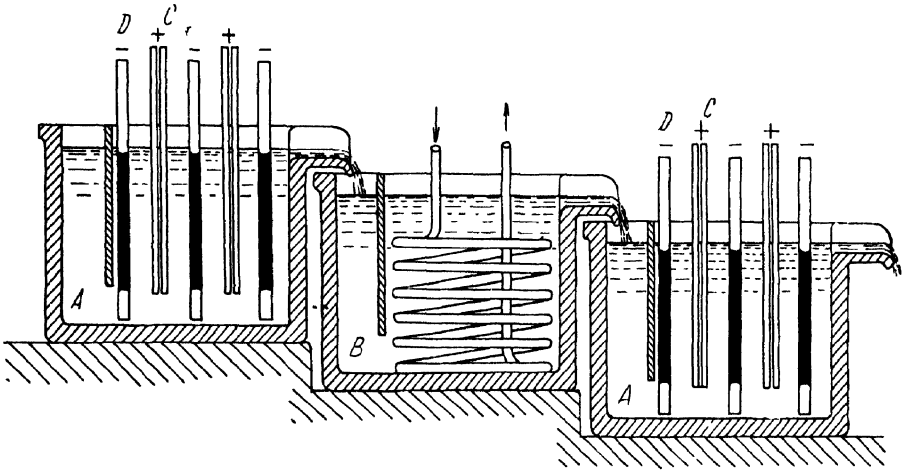


Fig. 129. Schuckert cell.
A — Electrolyzers, *B* — Brine coolers, *C* — Anodes (frames with platinum foils), *D* — Graphite cathodes.

sumption in spite of the fairly high voltage across the bath. To produce 1 kg of active chlorine in a solution containing 20 g Cl_2 per litre some 5.5 kw-hr. are required; the current efficiency is about 82 per cent, and the salt consumption around 7.5 kgs; if the bleaching liquor is to contain 35 g of Cl_2 per litre, some 7.1 kw-hr. are needed; current efficiency is 64 per cent and about 4.3 kg of salt are consumed. Fig 128 is a flow-sheet of a complete plant for the production of bleaching liquor.

Brine is pumped into tank *A* where the calcium and the magnesium salts are removed in order to prevent their deposition on the cathode. The brine is then decanted in tank *B*, flows to cooler *C* and is cooled by means of coil *D*. The cooled solution is then pumped to a small container *H*, in which a constant level is maintained; from there it flows down into electrolyzer *K*. After passing through the electrolyzer, it enters cooler *C* and is recirculated. As soon as the liquor attains the desired concentration, it is pumped into tank *O* by means of pump *G*.

b) *Schuckert cell*

The Schuckert cell (see Fig. 129) has proved more economical as far as the first costs for the platinum are concerned.

The electrolytical installation consists of a series of stoneware vessels fitted with overflows; the vessels are arranged in terraces so that the electrolyte flows through from one into another. The odd vessels are electrolyzers, the even ones are coolers with cooling coils of lead. Each electrolyzer is provided with a number of platinum anodes and graphite cathodes, which act as monopolar electrodes. The anodes are shaped like frames with a 0.02 mm platinum foil fixed on them. The voltage across the electrolyzer is 5.5 to 6 V; usually 18 to 20 such units are

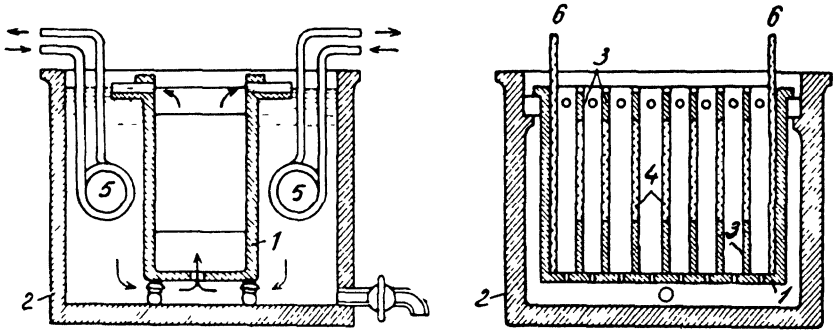


Fig. 130. Oettel-Haase electrolyzer.
1 — Inner stoneware vessel of electrolyzer, *2* — Outer stoneware vessel, *3* — Glass partitions, *4* — Graphite electrodes, *5* — Cooling coil, *6* — Current connection.

arranged in series, and the whole system is connected to 110 V mains. After the passage of the brine through the system (it is not circulated), a liquor is obtained containing some 20 g of active chlorine per litre. The starting electrolyte contains 110 to 150 g of NaCl per litre. A small amount of sodium resin soap is added to lower the reduction of hypochlorite at the cathode. To produce 1 kg of active chlorine (in solution containing 20 g of Cl_2 per litre) about 6.3 kw-hr. and 6 kgs of NaCl are required.

c) *Oettel-Haase electrolyzer*

The *Oettel-Haase* electrolyzer uses only graphite anodes (Fig. 130).

The stoneware vessel is provided with side grooves, into which bipolar graphite electrode plates between glass partitions are inserted. Each compartment thus formed is provided with bottom and side openings for the circulation of the electrolyte. The electrolyzer is placed on insulators in an outer larger stoneware vessel with a lead coil, through which the cooling water is pumped.

At the commencement of the operation, both the inner and the outer vessel are filled with brine up to the upper opening of the electrolyzer. As electrolysis

proceeds, the hydrogen liberated at the cathode lowers the specific weight of the electrolyte; as a result the brine flows through the upper openings of the inner vessel into the outer vessel, where the hydrogen is separated from it; the brine then sinks to the bottom and re-enters the electrolyzer through the hole in the bottom. In order to achieve better circulation the current density used is as high as possible (up to 14 A/sq. dm). The cooling coils maintain a temperature of 22 to 25 °C in the electrolyzer. As soon as the desired concentration is attained, the liquor is drained off through the bottom cock.

This electrolyzer consists of 28 to 30 chambers, and brine with 15 to 17 per cent sodium chloride is fed into them. The voltage across the chambers is about 3.7 to 4.2 V, so that the total voltage equals 106 to 126 V. This apparatus is simple in design and the first cost is comparatively low but it cannot be used for the preparation of liquors with more than 14 grams of active chlorine per litre. The current efficiency is also comparatively low, chiefly because of the low current density at the anodes, and the electrodes do no last for long. The energy required to produce 1 kg of active chlorine in a liquor containing 10 to 12 g per litre is about 6.5 kw-hr., while the consumption of salt is about 12 to 14 kg. A higher consumption of electrical energy is conduced, apart from the low current density, also by the short-circuit caused by parallel connection of the liquid in individual compartments. To suppress this, the electrolyte is led from the electrolyzer into the outer vessel by overflow tubes made as long as possible.

B. CHEMICAL PRODUCTION OF HYPOCHLORITE

Raw materials are: diluted hydroxide solution containing some 18—20 per cent of NaOH, and electrochemically produced chlorine (it is also possible to use tail gas, escaping from condensers in the liquefaction of chlorine). Chlorination proceeds in two immediately subsequent stages. At first, chloride and hypochlorous acid are formed:

$$NaOH + Cl_2 = NaCl + HOCl, \qquad \text{(XIII-19)}$$

the acid is immediately neutralized by hydroxide:

$$HOCl + NaOH = NaOCl + H_2O. \qquad \text{(XIII-20)}$$

The overall reaction can, therefore, be expressed as follows:

$$2\,NaOH + Cl_2 = NaOCl + NaCl + H_2O. \qquad \text{(XIII-21)}$$

According to this equation, an equivalent amount of hypochlorite and chloride should be formed. Hypochlorite, however, is a highly unstable substance and is easily converted into other products (see further); therefore, the liquor after chlorination always contains rather more chloride than hypochlorite.

During chlorination the heat liberated by the reaction must be removed to

prevent the temperature from exceeding 35 °C; failing this, the hypochlorite will decompose, mainly in presence of catalysts (such as compounds of iron, manganese, cobalt, nickel and chromium), according to the equation:

$$2\,NaOCl = 2\,NaCl + O_2. \qquad \text{(XIII-22)}$$

If an excess of chlorine is admitted into the hydroxide solution the hypochlorite will be converted into chlorate; the rate of this conversion is particularly high, if the temperature is allowed to exceed 40 °C. This reaction will be discussed later, when dealing with the preparation of chlorates. To prevent overchlorination the reaction must be interrupted before all the hydroxide is used up. The small amount of hydroxide which remains in the bleaching liquor will increase its stability during storage. It is also necessary to prevent local overchlorination of the hydroxide; this can be done if the chlorine is sufficiently diluted prior to its use.

Industrially the reaction is carried out in chlorination vessels either in batches or in continuously operating units. Absorption towers are rarely used.

In the batch process wide iron cylinders are used as chlorination vessels (of some 2.5 cubic meters content); the cylinders are rubber-lined and cooled by a coil made of rubber-lined steel or PVC. The vessels are filled with an 18 % hydroxide solution and the chlorine enters the solution through PVC pipes under cooling and stirring; the pipes end in distributors which are placed just above the bottom of the chlorination vessel. The vessels are closed by covers, and tail gases are sucked off and led above the roof of the building.

Chlorination is terminated as soon as the solution contains 12 % active chlorine and the hydroxide content has dropped to about 0.4 per cent. The liquor then flows into a vessel lined with tiles, where it is cooled and the impurities [$Fe(OH)_3$, $Mg(OH)_2$, $CaCO_3$)] are allowed to settle; if necessary, the composition is also adjusted.

In continuously working units cooled hydroxide solution enters at the bottom of the chlorinators which are provided with cooling coils; a measured amount of chlorine is simultaneously admitted. The hypochlorite solution leaves the vessels through the overflow, and flows through a stoneware coil, which is externally cooled by water, into a collecting tank with a rubber coated stirrer and a PVC water cooler. The composition of the liquor is here adjusted by the addition of hydroxide or chlorine, and the finished hypochlorite solution is then stored.

Absorption towers are used for preparation of hypochlorite liquors from diluted chlorine (25 to 40 per cent of Cl_2). The towers (2200 mm in diameter and 8000 mm in height) are made of rubber-lined steel. Raschig rings are arranged on a grid, under which the chlorine inlet tube is placed. A 20 per cent solution of sodium hydroxide enters from above through a distributing plate and is led out at the bottom from where it passes into a brick-lined steel cooler with stoneware coils, through which the water circulates. The liquid is then pumped from the cooler back to the top of the tower, until it has a content of

12 % active chlorine (i. e. 150 g of Cl_2 per litre). It is then led into a tank, where it is decanted and the composition adjusted.

No iron salts (or salts of other heavy metals) should be allowed to come into contact with the product either during the operation or when storing, as they cause it to decompose with the liberation of oxygen [see equation (XIII-22)]. For this reason it is better to use steam condensate for the preparation of the caustic solution instead of river water. Sodium hypochlorite prepared in this way is a solution which contains 150 grams of active chlorine per litre as well as 140 g of NaCl, 3 to 5 g of NaOH, 5 to 8 g of Na_2CO_3 and maximum of 0.01 g Fe.

The product is shipped in tank cars or in glass carboys. The solution must be stored cold and protected from sunlight. It is used for bleaching vegetable fibres, in laundries and textil factories. This hypochlorite solution is also used for the sterilization of water.

XIV. BLEACHING POWDER

Bleaching powder is a dry, whitish powder which smells of chlorine. It is obtained by the reaction of chlorine with hydrated lime. The product is not a uniform chemical compound, as its composition depends on the conditions under which it is prepared. In the air it is decomposed by the effect of moisture and carbon dioxide and is slowly transformed into a thick sludge. It usually contains 35 to 39 per cent active chlorine, after some time, however, the chlorine content will decrease. Its composition is usually expressed in the percentage of weight of active chlorine; in France, it is evaluated in the Gay-Lussac degrees, which express the number of litres of chlorine that can be set free from 1 kg of bleaching powder. When heated, a bleaching powder with less than 35 per cent chlorine will evolve oxygen. If a product with a higher active chlorine content is heated, chlorine and water will escape; at higher temperature chlorate will be simultaneously formed as an intermediary which decomposes and releases oxygen.

A. REACTIONS IN THE MANUFACTURE OF BLEACHING POWDER

The reaction mechanism accompanying the formation of the bleaching powder is not yet positively known. According to Ditz's opinion, the basic hypochlorite $CaO \cdot Ca\,Cl\,(OCl) \cdot H_2O$ is formed at lower temperature in accordance with the following reaction:

$$2\,Ca(OH)_2 + Cl_2 = CaO \cdot Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix} \cdot H_2O + H_2O. \qquad \text{(XIV-1)}$$

At higher temperatures the compound $Ca\,Cl\,(OCl) \cdot H_2O$ will arise:

$$CaO \cdot Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix} \cdot H_2O + H_2O = Ca\,(OH)_2 + Ca\begin{matrix}\diagup Cl \\ \diagdown OCl\end{matrix} \cdot H_2O. \qquad \text{(XIV-2)}$$

The calcium hydroxide which is simultaneously formed will in turn react with the chlorine according to the first reaction, so that the final product will be a mixture of the compounds

$$CaO \cdot Ca\begin{matrix}\diagup OCl \\ \diagdown Cl\end{matrix} \cdot H_2O + Ca\begin{matrix}\diagup Cl \\ \diagdown OCl\end{matrix} \cdot H_2O.$$

By his theory Ditz accounts for the formation of free reaction water, further for the presence of hydrate water, for the variable composition of the bleaching

powder (especially the possibility of preparing a bleaching powder with a high content of active chlorine), and ultimately for the presence of free, unchlorinated calcium oxide.

According to Bunn and Clark, a mixture of basic hypochlorite $Ca(OCl)_2 \cdot 2\,Ca(OH)_2$ with basic calcium chloride $CaCl_2 \cdot Ca(OH)_2 \cdot H_2O$ is formed during the first chlorination stage. As the reaction proceeds the basic hypochlorite will be further chlorinated and converted into a less basic salt $3\,Ca(OCl)_2 \cdot 2\,Ca(OH)_2 \cdot 2\,H_2O$, while the composition of the basic calcium chloride remains unchanged.

At a still later stage of chlorination, the basic hypochlorite will be ultimately decomposed and converted into neutral calcium hypochlorite $Ca(OCl)_2 \cdot 3\,H_2O$. The final product of the reaction of chlorine with slaked lime is, therefore, a mixture of neutral calcium hypochlorite, basic calcium hypochlorite, and basic calcium chloride. The mutual ratio of these components will depend on the operating conditions under which the chlorination is carried out.

Up to now it has not been finally decided which view mentioned above is correct regarding the reaction which takes place during the chlorination of lime. Industrially, bleaching powder is usually considered to be a compound CaCl (OCl), without, however, attributing to this formula other than a merely qualitative meaning.

When preparing bleaching powder, the temperature must be kept below 45°C, in order to prevent the product becoming "overheated" due to the reaction:

$$6\,CaCl\,(OCl) = Ca\,(ClO_3)_2 + 5\,CaCl_2. \qquad \text{(XIV-3)}$$

The presence of iron and manganese compounds in the raw materials is detrimental, causing catalytic decomposition of bleaching powder as follows:

$$2\,CaCl\,(OCl) = 2\,CaCl_2 + O_2. \qquad \text{(XIV-4)}$$

Water is an important reaction component and increases the reaction rate. (Completely dry chlorine and dry calcium hydroxide hardly react at all and the chlorine is merely absorbed). For this reason slaked lime is generally used (e. g. for operation in the chambers and in Hasenclever's apparatus) containing a certain amount (4 to 6 per cent) moisture. In the Backmann apparatus calcium hydroxide with only a very low moisture is used so the chlorination rate is lower, despite the fact that the lime during the reaction is continually raked up by the stirring device.

B. RAW MATERIALS FOR THE MANUFACTURE OF BLEACHING POWDER

The chlorine used in the manufacture of bleaching powder should be dry and contain as maximum 2 per cent carbon dioxide, as this converts lime into carbonate. If the content of hydrogen present in the chlorine exceeds 4 per cent, an explosion may occur; apart from this, it also reacts with the bleaching

powder, causing hydrogen chloride to be formed, which reduces active chlorine content. For manufacture, either chlorine containing tail gas from the liquefaction station is used or chlorine produced by electrolysis, which is diluted with air to the concentration required for the given type of equipment.

The lime must not contain any compounds of iron and manganese, as they promote the decomposition of the bleaching powder both during manufacture and storing; apart from this, the product becomes red. The presence of magnesium oxide is undesirable, as magnesium hypochlorite is easily decomposed into chloride, which makes the product hygroscopic and incapable of storage. A higher content of silicon dioxide results in the so called "meagre" lime, which is difficult to slake and absorbs chlorine at a slow rate. Aluminium oxide makes it difficult to clarify the bleaching powder solutions. Apart from this, it is a ballast, similarly to silicon dioxide. The lime should not contain any calcium sulphate or undecomposed carbonate, as these compounds reduce the content of free CaO. The optimum temperature for the burning of limestone is between 1000 and 1100 °C. If lime is not properly burnt, it will be sufficiently reactive, but will contain pieces of undecomposed limestone. If, however, the lime is overburnt (dead burnt) hydration will be difficult and the slaked lime obtained will not be sufficiently reactive. Overburnt lime differs in appearance from the normally burnt lime. It is darker having a greyisch or greenish tinge with a surface wrinkled by cracks, and its weight is higher. Lime suitable for the production of bleaching powder should contain no more than 1 per cent MgO, 1 per cent SiO_2, 0.1 per cent Fe_2O_3, 0.5 per cent Al_2O_3 and 1.3 per cent $CaCO_3$ plus $CaSO_4$.

Generally, lime is slaked in a Schulthess slaker. This consists of a stationary horizontal cylinder, in which a bladed shaft revolves. In the front, there is a perforated drum, which rotates with the shaft Quicklime is charged through a funnel and simultaneously water 90 °C hot is introduced into the drum. While the lime slakes, it disintegrates into powder and falls through the screen of the rotating drum into the external cylinder. Rotating blades carry the powder to an outlet at the other end of the slaker. Impurities such as sand or coke are retained in the screen and periodically removed. The heat released during slaking evaporates a part of the water and the vapour together with the entrained fine powder escapes into a stack directly connected with the slaker. In the stack, a shower of water condenses the water vapour and holds the dust which escapes from the slaker. During this procedure water is heated to about 90 °C, and flows to the slaking drum.

The slaked lime used in the production of standard bleaching powder should contain about 4 to 6 per cent moisture, and it should be free of clods and any foreign bodies. In order to meet these requirements the lime, after passing through the slaker, is ground in a disintegrator and screened in a rotating screen. At this stage, the hydrated lime still contains a certain amount of unhydrated oxide, which is undesirable for two reasons. Firstly the calcium oxide will not combine with the chlorine and behaves as an inert substance,

which reduces the active chlorine content in the final product. Secondly some oxide clods will be hydrated only during subsequent chlorination, from which results a local overheating and decomposition of the bleaching powder.

Therefore, the lime is allowed to mature for one to three weeks, so as to become completely slaked and also that the moisture will be evenly spread. The lime enters the storage bunker at a temperature of 80 °C. After maturing, the temperature will be about 30 °C.

The chlorination of hydrated lime is carried out in chambers or in mechanical devices.

C. STANDARD BLEACHING POWDER

1. Manufacture of bleaching powder in chambers

The chambers are made of concrete or of welded lead sheets. The inside is coated with a bituminous paint. Lead chambers are preferred because of their higher heat conductivity. They are fixed in a steel structure (similar to chambers used for the production of sulphuric acid) and are generally 1.2 to 2.5 m

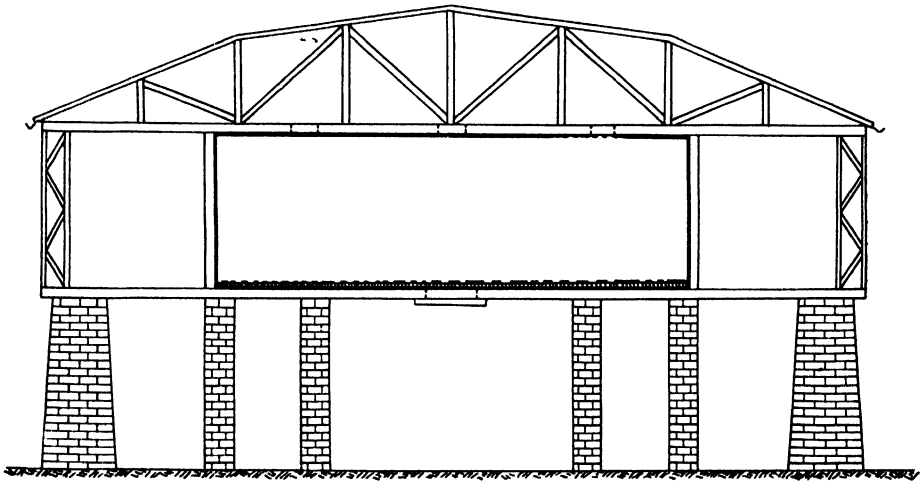


Fig. 131. Chamber for the manufacture of bleaching powder.

high, 10 to 20 m long and 7 to 12 m wide. As a rule, they are erected on columns 2 to 3 m high so that it is possible to empty the chamber from the base (see Fig. 131).

The chambers are usually located below the roof to keep a a uniform temperature. A unit consists of four to six chambers. Three to five chambers connected in series are under operation, one chamber is filled and the last is emptied.

Chlorine diluted with air is introduced in the front of the chamber and let out at the opposite end. The lime charging openings are in the ceiling while in

the bottom are openings with lids for the discharge of the finished product. At the side of the chamber is a wooden door with a lead coating for the operators to enter the chamber and remove the product.

At first, the chlorine is led into the chamber filled with a nearly finished product, passes through the other chambers, and is drawn off from the last chamber filled with fresh lime. The lime containing 4 to 6 per cent moisture covers the bottom of the chamber in a layer of 3 to 10 cm. If the layer is 10 to 20 cm, the lime must be raked during chlorination, which is a very straining and unhealthy procedure. The chambers operate under a slight vacuum so that the chlorine will not escape into the ambient atmosphere. The course of chlorination is checked according to the composition of the samples of gas, which are drawn from the sampling cocks in the walls of the chambers. A rising concentration of gas shows that absorption is decreasing and the reaction is almost at an end. As soon as chlorine absorption has ceased, the remaining gas is expelled from the chamber by air from a fan into another chamber filled with a fresh charge of lime, or into a tower which is sprayed with milk of lime. The chamber door is opened for airing. The bleaching powder is shoveled into wooden or steel drums for transportation. The empty chamber is refilled with fresh lime. The time of chlorination process depends upon a number of factors: the thickness of the layer of fresh lime, the temperature, the humidity of the lime, and the chlorine content in the gas. It, therefore, varies widely from 20 to 80 hours.

If high quality bleaching powder containing 35 to 36 per cent active chlorine is required, the temperature in the chamber must not be higher than 40 °C. A higher temperature will accelerate the chlorination process but also may cause overchlorination, particularly towards the end of the process, resulting in the formation of chlorate. The temperature in the chambers can be reduced either by diluting chlorine with a greater amount of air, or by inserting cooling coils at the bottom of the chamber, or by protecting the chambers from the direct effect of the sunrays. It is also necessary to avoid excessive moisture in lime as it causes clods to be formed which are chlorinated only on the surface and enclose unreacted lime in the centre. The more water the product contains, the less stable it is.

An operator's work in chambers is very unhealthy, particularly when removing the finished product from the chambers during which gas masks must be worn. It is no wonder that efforts have been made to mechanize this unpleasant manual work. Today, practically all over the world the manufacture of bleaching powder is mechanized and chambers are a thing of the past.

2. The manufacture of bleaching powder according to Hasenclever process

Apparatus (see Fig. 132) consists of four to eight superposed cast iron cylinders B, C ..... G, 4 metres long, connected by overfalls.

Each cylinder has a stirrer with cast steel blades, which gradually push the slaked lime entering from the charging hopper *A* into the next lower cylinder. Chlorine is led into the second lowest cylinder from the side at *K* and comes into contact with the almost finished bleaching powder. As the process continues, the chlorine comes into contact with a weaker and weaker bleaching powder until in the end very diluted chlorine passes through the pure lime, so

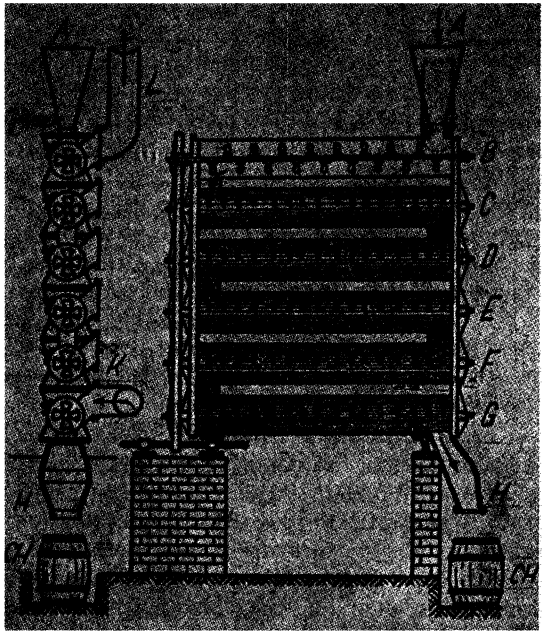


Fig. 132. Hasenclever's mechanical equipment for bleaching powder manufacture. *A* — Slaked lime hopper, *B*, *C*.....*G* — Cast iron cylindres, *H* — Bleaching powder discharge, *CH* — Barrels for finished product, *K* — Chlorine inlet, *L* — Tail gas outlet.

that the gases leaving the chlorinator by a tube *L* are almost free of chlorine. In the front of the lowest cylinder the finished bleaching powder is discharged into a barrel. The air which is required to dilute the chlorine is introduced into the bottom cylinder. At the same time the air removes the absorbed chlorine from the bleaching powder. The ratio of the two gases is controlled so as to obtain a 10 to 12 per cent chlorine mixture. The stirring device is driven by cog wheels located at the side of the apparatus. All the equipment is made of cast iron and has a protective coating of paint against the corrosive effect of chlorine. At the chlorine inlet, the temperature is about 25 °C and rises to 45—50 °C in the middle cylinders, dropping slightly to 40—45 °C nearer the outlet.

Hasenclever's apparatus has many advantages as compared to the chamber system. It is rather small, requires less manual work, and the health of the operators is not threatened by the chlorine, which escapes into the atmosphere. A drawback is the rather low output caused by the insufficiently quick removal of the reaction heat which makes it impossible to use more concentrated chlorine. The periodical cleaning of the cylinders from sediments as well as repair of the equipment involves frequent interruptions of the operation.

The finished bleaching powder usually contains 36 to 39 per cent total chlorine, 35 to 37 per cent active chlorine, 2 to 4 per cent calcium chloride, 0.5 per cent calcium chlorate, 2 to 3 per cent calcium carbonate, 8 to 16 per cent free calcium hydroxide, 0.05 to 0.15 per cent iron, 5 to 8 per cent moisture and 12 to 18 per cent total water. The product is not stable and the chlorine content gradually decreases. After being stored for 70 days, the average active chlorine loss amounts to some 11 per cent, after 120 days it reaches some 14 per cent. In order to reduce losses it is necessary to store the bleaching powder in a cool and dry place.

D. STABLE BLEACHING POWDER

Bleaching powder manufactured in chambers or in Hasenclever's apparatus is not stable and in the course of time the active chlorine content diminishes due to the following reactions:

$$2\ CaCl(OCl) = 2\ CaCl_2 + O_2, \qquad \text{(XIV-5)}$$

$$CaCl(OCl) + H_2O = Ca(OH)_2 + Cl_2 \qquad \text{(XIV-6)}$$

The first reaction is promoted by catalysts (iron and manganese salts) and by a high temperature. The second reaction, which is the most important with regard to decomposition, is due to the presence of water in the product (it usually contains 5—8 p. c. of water). The amount of water can be reduced if fresh moist bleaching powder is mixed with the unhydrated quicklime. This reacts with the moisture in the product and changes into hydroxide. This mixture of bleaching powder, having an admixture of 75 per cent lime, used to be marketed as a stable product ("20 per cent bleaching powder"). Today, we understand a stable bleaching powder to be one with an active chlorine content, which even after five years storage will not be less than 35 per cent.

1. Manufacture of a stable bleaching powder by the Backmann method

Stable bleaching powder is produced according to Backmann's method by using slaked lime with a minimum of moisture (which must not exceed 0.5 per cent) for the process. Also chlorine must be free of any moisture.

Chlorination is carried out in tall, reinforced concrete towers protected inside by a bituminous coating (see Fig. 133).

The tower consists of two chambers, each of them having six to eight floors. The cross section is octagonal or circular. A shaft carrying arms with blades passes through the center of each chamber. Screened slaked lime is transported from the storage tanks h_1, h_2 by means of automatic feeders k_1, k_2 to scales i_1, i_2 and then discharged on the second floor (powder entrained with the gas settles on the first floor). The arms of the slowly revolving stirrer transport the slaked lime to the centre of the chamber, where the lime then falls down on the lower

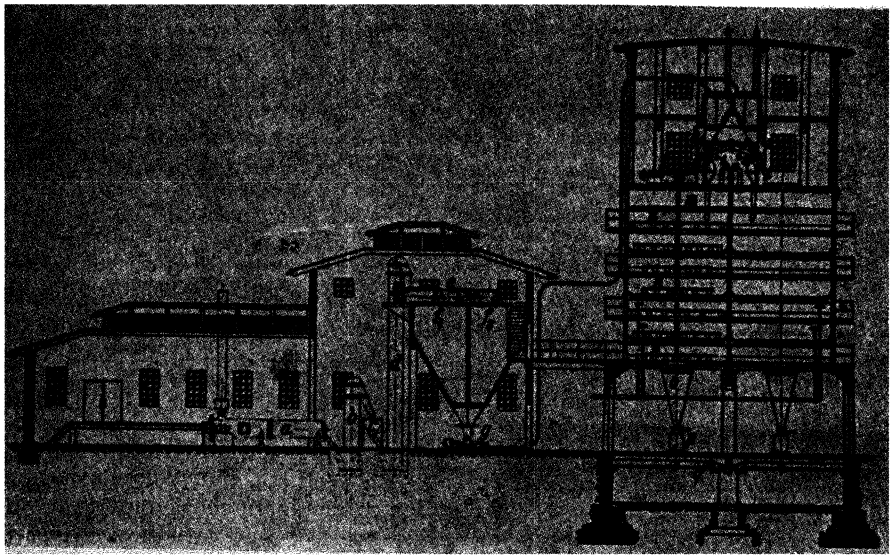


Fig. 133. Manufacture of bleaching powder by the Backmann method.
a — Slaker for hydrated lime manufacture, *b* — Elevator, *c* — Slaked lime screen, *d* — Elevator, *e* — Worm-transporter, f_1 f_2 — Slaked lime bunkers, *g* — Equipment carrying slaked lime to storage tanks, h_1, h_2, — Storage bunkers, k_1, k_2, — Automatic feeders, i_1, i_2, — Automatic scales, *n* — Floors provided with raking equipment, *o* — Bleaching powder discharge, *p* — Filling of bleaching powder into barrels, *q* — Vibrator.

floor. Then the lime is transported to the perimeter and again falls in turn to the floor below. The chlorine is introduced into the second floor from below. Dry cold air enters the lowest floor in order to remove the absorbed chlorine from the product. The bleaching powder is dropped into container *o*, from where it is filled into barrels *p*. The content of the barrels is vibrated by a device *q*. The tail gas, which still contains some 0.2 per cent of unabsorbed chlorine, is drawn off by a fan and passes through an absorption tower, scrubbed with milk of lime.

During chlorination the highest temperatures of 35 to 40 °C is reached on the middle floor, while on the bottom floor a temperature of approximately

20 °C is maintained. With regard to the thermal unstability of the bleaching powder during the last production stage chlorination is completed at low temperatures. On the other hand chlorination of fresh or only partly chlorinated lime does not involve a sensitive operation. So the higher temperature on the middle floor is used to accelerate the reaction. The colour of the gas is observed and temperatures are measured to supervise the course of the reaction. A rise in temperature on the lower floors signifies that an insufficient amount of chlorine has been introduced, while a higher temperature on the upper floors signifies that too much chlorine has been introduced and so the amount of lime must be increased. Cooling coils are embedded in each floor to control the temperature.

The Backmann apparatus is manufactured by the Krebs factory for a daily output of 3 to 5 tons of bleaching powder.

2. Manufacture of stable bleaching powder according to Moore

In this case reaction between the lime and the diluted chlorine takes place in a revolving drum about 40 m long and 1.5 m in diameter, lined with bricks. Therefore, the lime when passing through the drum is not contaminated with the iron, which may cause decomposition of the product. At one end, the slaked lime is introduced by a worm and the finished product is discharged at the other end. The rotating drum is set at a slight angle and the inside walls are fitted with ribs. Both these measures assist in pushing the material forward. Chlorine gas is circulated through the system in a closed circuit. The gas which enters at the bottom of the drum contains 11 to 17 per cent chlorine, while on leaving the drum only 4 to 7 per cent. For this reason both ends of the drum are closed by cast iron lids, which have openings for lime feeding and the discharging of the bleaching powder, as well as a chlorine inlet and outlet. The gases leave from the top of the drum at a temperature of 70 to 80 °C and are first cooled in stoneware air coolers, in which a portion of the water vapour formed during the reaction is simultaneously condensed. In the cooler, the dust entrained in the gas stream is also separated. At the end of the cooler there are two connections attached to the gas main. A part of the circulating gas is taken off by the first piping as the gas has been diluted by the air which has penetrated into the drum owing to a slight vacuum. The second connection serves to introduce a further amount of fresh chlorine, so as to increase its content in the gaseous mixture to the required 14 to 17 per cent. The gas is drawn off by means of a circulating stoneware fan and passes through lead pipes, which are cooled externally with brine. Here the temperature is decreased to about 7 °C in order to condense more of the water evaporated during the reaction in the drum. To lower the temperature below this limit is undesirable as it would cause the solid octahydrate $Cl_2 . 8H_2O$ to be separated. On leaving the brine cooler, the gas passes through a series of quartz pipes which are externally heated by oil burners and its temperature is raised to approx. 120 °C. The hot

gas then enters the bottom of the revolving drum and passes up to the feed and countercurrently to the lime. The stable bleaching powder is taken out at the lower end at an approximate temperature of 60 to 70 °C.

Moore's equipment is designed with the knowledge that the presence of a certain amount of water accelerates the reaction of chlorine with lime. But a moist, sticky raw material is difficult to transport; moreover, it clogs the screens of the hydrator, impedes the movement of the worm conveyors and causes the shafts to break, etc. To avoid these difficulties the process does not start with moist slaked lime but with dry material and the water needed to accelerate the reaction (5 to 7 per cent) is immediately sprayed into the drum through an atomizer. Added water also reduces the reaction temperature, thus preventing the product from overheating, which can occur as a result of a high rate of the chlorination in the rotating drum. The water, after taking part in the reaction, is quickly evaporated and carried away from the reaction zone by circulating gas.

The finished product contains only 1 per cent moisture, some 39 per cent total chlorine, 36 per cent active chlorine, 5 per cent calcium chloride and 0.8 per cent calcium chlorate.

Standard bleaching powder can also be manufactured in Moore's drum if the quartz preheater for circulating gases is out of operation. In this case a smaller quantity of water is evaporated in the drum; the water content in the final product is then about 5 per cent. Since during the manufacture of this product the temperature attained in the reaction zone of the drum is lower so the hypochlorite is decomposed to a lesser degree than when manufacturing a stable bleaching powder. Therefore, the product contains less calcium chloride (max. 4 per cent) and less calcium chlorate (max 0 5 per cent); also fresh standard bleaching powder has a somewhat higher content of active chlorine (about 37 per cent).

A stability test is made after 2 hours drying at 100 °C in order to ascertain the drop in active chlorine content. A stable product manufactured in Moore's equipment shows a loss of 3.5 per cent while an unstable product about 14 per cent. From this we can see that although decomposition is suppressed to a considerable extent in the case of a stable product, the active chlorine loss is still noticeable. The so called "superstable bleaching powder" is prepared by the addition of quick lime to the stable product. A stability test then shows active chlorine loss to be less than 0.75 per cent.

Bleaching powder is packed in well sealed wooden barrels or in sheet iron drums. It is used mainly to bleach fabrics in the textile industry and cellulose in the paper industry. Bleaching powder is also a well known disinfectant and is used in purifying water for municipal purposes. Certain quantities are used for oxidation reactions in organic chemistry, for instance in the production of chloroform. The stable product is exported mainly to tropical countries.

XV. CALCIUM HYPOCHLORITE

Efforts to produce a bleaching powder in a more concentrated and stable form resulted in the manufacture of calcium hypochlorite $Ca(O\,Cl)_2$. In pure form it contains 99.2 per cent active chlorine. It is manufactured in various ways and sold commercially under different names, e. g. "Perchloron" produced by I. G. Farben, "H. T. H." by Mathieson Alkali Works, "Pittchlor" by Pittsburg Plate Glass Co., Columbia. Chemical Division.

Perchloron contains 60 to 70 per cent active chlorine, 1 to 2 per cent water, the remainder being calcium hydroxide and chloride. The I. G. Farben method starts with a thick lime slurry, containing some 30 per cent CaO, which is chlorinated in horizontal cylindrical drums (about 1.7 m in diameter and 3 m long). The drums equipped with stirrers are submerged in water. Chlorination is carried out under pressure and at a temperature not exceeding 40 °C by liquid chlorine, which is introduced above the surface of the slurry.

Reaction proceeds according to this equation:

$$2\,Ca\,(OH)_2 + 2\,Cl_2 = Ca\,(OCl)_2 + CaCl_2 + 2H_2O. \qquad \text{(XV-1)}$$

The quantity of water used in the reaction must be sufficient to ensure that calcium chloride remains in the solution, whilst calcium hypochlorite is precipitated as a solid substance. Filtration is very difficult and is carried out by means of a special hydraulic press which operates under a pressure of 150 atm. sq. cm. Stainless steel gauze is used as a filter cloth.

The filter cake, which contains about 8 per cent $CaCl_2$, 12 per cent CaO, 54 per cent active chlorine and 25 per cent water, is crushed and dried in two process stages. In the course of the first drying stage, performed in the Buehler apparatus, the moisture is reduced from 25 to 6 per cent. Air preheated to 180 °C is allowed to flow through two vertical pipes connected in series, 0.5 m in diameter, 12 m high. Rapidly circulating air entrains wet powder, which is dried on its passage through the pipes. A partly dried product is then separated from the air in a cyclon, and the drying process is completed in a horizontal dryer equipped with a steam-jacket. Air from the cyclon is led through an electrostatic precipitator, in order to catch the entrained dust.

The mother liquor leaving the hydraulic filters, containing up to 100 g of active chlorine and 260 g of chloride ion per litre, is converted into a monohydrate $Ca\,Cl_2 . H_2O$. After nickel salt, acting as catalyst, has been added, the present hypochlorite is decomposed at an elevated temperature. Then chlorate will be reduced by sulphur dioxide. The solution obtained is filtered and sprayed by atomizers into a spray dryer where it is dried by hot air and converted into dry calcium chloride powder ($CaCl_2 . H_2O$).

Mathieson Alkali Works eliminate the difficulties connected with the filtration of calcium hypochlorite by chlorinating the lime sludge in the presence of

sodium hydroxide. A ternary salt $Ca(O\,Cl)_2$. $NaOCl$. $Na\,Cl$. $12\,H_2O$ is crystallized by successive cooling of the sludge to 10°C. The salt is easy to filter. It is then allowed to react with a specialy prepared chlorinated lime slurry in a proportion corresponding to the equation:

$$2Ca\,(OCl)_2 \cdot NaOCl \cdot NaCl \cdot 12\,H_2O + CaCl_2 + Ca\,(OCl)_2 = 4Ca\,(OCl)_2 \cdot 2H_2O + \\ + 4\,NaCl + 16\,H_2O. \qquad \text{(XV-2)}$$

The precipitate is then filtered and the paste obtained is either dried under reduced pressure to a granulated product, or spray-dried in hot air to a powder.

In the Columbia process chlorine diluted with air and carbon dioxide is passed through solid sodium carbonate or bicarbonate. In the reaction chlorine monoxide is formed according to the equation:

$$2\,Cl_2 + 2\,NaHCO_3 = Cl_2O + 2\,NaCl + 2\,CO_2 + H_2O. \qquad \text{(XV-3)}$$

The diluted gas obtained is led through ice-cold water, in which the chlorine monoxide will dissolve, and an approx. 10 to 15 per cent solution of hypochlorous acid will be formed:

$$Cl_2O + H_2O = 2\,HOCl. \qquad \text{(XV-4)}$$

The hypochlorous acid will then be neutralized with lime at a low temperature:

$$Ca\,(OH)_2 + 2\,HOCl = Ca\,(OCl)_2 \cdot 2\,H_2O \qquad \text{(XV-5)}$$

The solution obtained is filtered and dried by hot air in spray dryers.

The advantage of calcium hypochlorite, compared to standard bleaching powder, is a higher content of active chlorine. Moreover, it forms clear solutions in water and is much more stable particularly at higher temperatures. After 5 years storage in tropical countries, chlorine content will not drop below 55 per cent. Another advantage of the calcium hypochlorite is that it is less hygroscopic due to a lower content of calcium chloride.

XVI. SODIUM CHLORITE

The sodium salt of chlorous acid $HClO_2$ was introduced onto the market as a modern bleaching article in 1940. Decomposition of this salt by hydrochloric acid proceeds according to the following equation:

$$NaClO_2 + 4\ HCl = NaCl + 2\ H_2O + 2\ Cl_2. \qquad \text{(XVI-1)}$$

From this it can be seen that 100 g of chlorite are equivalent to 156.99 g of active chlorine. The commercial product which has some 80 per cent $NaClO_2$ therefore contains 125 per cent active chlorine.

Chlorite is known in two forms: $NaClO_2$ and $NaClO_2 . 3\ H_2O$. The powder is completely stable, if stored in a dry place and at a normal temperature. When heated up to 150 to 200 °C, it decomposes mainly into chlorate and chloride and to a lesser extent into oxygen and chloride. Chlorite is more stable than hypochlorite, but less stable than chlorate. Its reaction with sulphur is spontaneous. It is, therefore, imperative to prevent chlorite from coming into contact with rubber which had been vulcanized with sulphur.

Sodium chlorite readily dissolves in water. At 17 °C a saturated solution contains 39 per cent $NaClO_2$, at 30 °C 46 per cent $NaClO_2$. Its neutral or weak alkaline solutions are also stable; when brought to the boil, they will slowly decompose. In a cold alkaline solution, chlorite acts as a very mild oxidizing agent. However, the oxidizing power increases considerably after heating or in an acid solution. After treating with sulphuric acid the very unstable chlorous acid is liberated from the chlorite Chlorous acid decomposes, forming chlorine dioxide according to the equation:

$$4\ NaClO_2 + 2\ H_2SO_4 = 2\ Na_2SO_4 + 4\ HClO_2, \qquad \text{(XVI-2}$$

$$NaClO_2 + 4\ HClO_2 = NaCl + 2\ H_2O + 4\ ClO_2, \qquad \text{(XVI-3)}$$

$$5\ NaClO_2 + 2\ H_2SO_4 = 2\ Na_2SO_4 + NaCl + 2\ H_2O + 4\ ClO_2. \qquad \text{(XVI-4)}$$

Chlorine dioxide is also set free, if chlorine is introduced into a concentrated chlorite solution:

$$2\ NaClO_2 + Cl_2 = 2\ NaCl + 2\ ClO_2. \qquad \text{(XVI-5)}$$

The manufacture of sodium chlorite starts from chlorine dioxide ClO_2. It can easily be prepared in a laboratory by heating a mixture of powdered potassium chlorate and oxalic acid to 70 °C. The gas escaping will contain carbon dioxide and chlorine dioxide.

$$2\ HClO_3 + H_2C_2O_4 = 2\ CO_2 + 2\ H_2O + 2\ ClO_2. \qquad \text{(XVI-6)}$$

From the gaseous mixture obtained chlorine dioxide can be separated by liquefying in a tube which is cooled by a freezing mixture. It is a deep red liquid boiling at 11 °C. A water solution is prepared by introducing the above gas into water, in which the chlorine dioxide will be absorbed, whilst the major part of the carbon dioxide will escape.

Chlorine dioxide can also be manufactured by introducing a gaseous mixture of sulphur dioxide and air into a solution of sodium chlorate and sulphuric acid

$$2\ NaClO_3 + 2\ H_2SO_4 = 2\ HClO_3 + 2\ NaHSO_4, \qquad \text{(XVI-7)}$$

$$2\ HClO_3 + SO_2 = 2\ ClO_2 + H_2SO_4. \qquad \text{(XVI-8)}$$

Chlorine is a by-product of this reaction and is formed according to equations:

$$2\ HClO_3 + 6\ SO_2 + 6\ H_2O = 2\ HCl + 6\ H_2SO_4, \qquad \text{(XVI-9)}$$

$$HClO_3 + 5\ HCl = 3\ Cl_2 + 3\ H_2O. \qquad \text{(XVI-10)}$$

An industrially important method of manufacturing chlorine dioxide is the decomposition of calcium chlorate by hydrochloric acid (see later Mathieson production method).

In the second stage of production the chlorine dioxide is converted into chlorite. This conversion can be carried out by hydrolysis in an alkaline solution, according to the equation:

$$2\ ClO_2 + 2\ NaOH = NaClO_2 + NaClO_3 + H_2O. \qquad \text{(XVI-11)}$$

These two products, chlorite and chlorate, can be separated by crystallisation. Fractional crystallisation can be performed easily if chlorine dioxide is absorbed in a solution of equivalent amounts of sodium and potassium hydroxide. After absorption has been completed, a solution of sodium chlorite and potassium chlorate is obtained. These two salts can easily be separated as sodium chlorite dissolves far more readily in water than potassium chlorate.

More economical than the above mentioned method are processes in which the chlorine dioxide is absorbed in a solution of sodium hydroxide in the presence of a suitable mild reducing agent, which reduces chlorine dioxide to chlorite only. This reaction proceeds according to the equation:

$$ClO_2 + e = ClO_2^-. \qquad \text{(XVI-12)}$$

The best reducing agent is hydrogen peroxide as it ensures a very high chlorite yield:

$$2\ ClO_2 + H_2O_2 + 2\ NaOH = 2\ NaClO_2 + 2\ H_2O + O_2. \qquad \text{(XVI-13)}$$

However, because of the high price of hydrogen peroxide this simple and easy method cannot be exploited commercially.

During the war I. G. Farben made experiments to reduce chlorine dioxide by zinc dust dispersed in water:

$$2\ ClO_2 + Zn = Zn\ (ClO_2)_2. \qquad \text{(XVI-14)}$$

The zinc chlorite obtained was finally converted by sodium hydroxide into sodium chlorite, zinc hydroxide being the by-product. After filtration the sodium chlorite solution was concentrated, crystallized, and the crystalline product dried. But the yield was not very satisfactory, as the reduction power of zinc is too high. Regarding this, lead monoxide in an alkaline solution appears to be a more suitable reducing agent. The reaction proceeds according to the summary equation

$$2\ ClO_2 + PbO + 2\ NaOH = 2\ NaClO_2 + PbO_2 + H_2O. \qquad (XVI\text{-}15)$$

Lead dioxide is formed as a by-product, which can easily be separated from the sodium chlorite solution by filtering.

The Mathieson Alkali Works manufacture chlorite for commercial use in the following way. The lime sludge is chlorinated at an elevated temperature, which results in the formation of chlorate:

$$6\ Ca(OH)_2 + 6\ Cl_2 = Ca\ (ClO_3)_2 + 5\ CaCl_2 + 6\ H_2O. \qquad (XVI\text{-}16)$$

The calcium chlorate is then treated with hydrochloric acid at a low temperature:

$$Ca(ClO_3)_2 + 4\ HCl = CaCl_2 + 2\ ClO_2 + Cl_2 + 2\ H_2O. \qquad (XVI\text{-}17)$$

The liberated mixture of chlorine dioxide and chlorine is diluted with air and allowed to react with lime, which combines preferentially with the chlorine and gives calcium chlorate according to equation (XVI-16). The remaining chlorine dioxide is then absorbed in sodium hydroxide in the presence of carbon, which acts as a moderate reducing agent (e. g. animal charcoal), and in the presence of lime:

$$4\ NaOH + Ca\ (OH)_2 + C + 4\ ClO_2 = 4\ NaClO_2 + CaCO_3 + 3\ H_2O. \qquad (XVI\text{-}18)$$

The calcium carbonate is filtered off, then the chlorite solution is evaporated and the crystalline product dried.

Sodium chlorite is used for bleaching mainly in the paper industry. A noteworthy advantage of this product is its ability to bleach paper pulp up to intense whiteness, without affecting the mechanical strength of the cellulose fibres. As chlorite is rather expensive, pulp is usually first bleached by hypochlorite as long as there is no risk of damage to the fibres, and then the bleaching process is completed by the chlorite. Chlorite is also an excellent bleaching agent for cotton and artificial fibres. It is also used to bleach wood, straw, ramia, hemp etc. Sodium chlorite is also used as raw material for the preparation of chlorine dioxide. In this case a mixture of chlorine and air is led through a layer of sodium chlorite containing 2 to 5 per cent moisture. The chlorine dioxide thus obtained is strongly diluted by air and used to bleach flour or paper pulp. It can also be used as a fungicide when preserving fruit. Regarding its oxidizing power one molecule of chlorine dioxide is equivalent to 2.5 chlorine molecules.

XVII. CHLORATES

Potassium chlorates and sodium chlorates are technically the most important salts of chloric acid. Potassium chlorate $KClO_3$ crystallizes in the monoclinic system. The crystals are colourless, with a glassy appearance, and according to the conditions under which crystallization takes place, they assume either the shape of fine needles or scales. Their solubility in water is low and largely depends on the temperature. When heated to or above the melting point, potassium chlorate decomposes and oxygen is evolved. If rubbed with organic substances, it explodes. Textiles impregnated with potassium chlorate will readily catch fire. Potassium chlorate like other chlorates is poisonous.

Sodium chlorate $NaClO_3$ forms colourless crystals of the cubic system and easily dissolves in water. In moist air the crystals absorb water and form a solution. The chemical properties of sodium chlorate are similar to those of potassium salt.

Chlorates can be obtained either chemically or electrochemically.

A. CHEMICAL MANUFACTURE OF CHLORATES

Chlorates are formed by introducing chlorine into a warm alkali hydroxide solution. The reaction can be divided into two stages. In the first stage the chlorine is hydrolysed into hypochlorous acid, which is immediately neutralized by the hydroxyl ions and hypochlorite is formed, so that the overall reaction is expressed by the following equation:

$$Cl_2 + 2\ OH^- = ClO^- + Cl^- + H_2O. \qquad \text{(XVII-1)}$$

In order to prevent the hypochlorite decomposing into oxygen and chloride, it is necessary, at this stage of chlorination, to maintain a lower temperature, and to avoid the presence of all catalytically active substances, especially compounds of iron, nickel, cobalt and manganese.

The second chlorination stage starts when further amounts of chlorine are introduced into the solution, until all hydroxyl ions are consumed. Therefore, the hypochlorous acid formed will not find any more hydroxyl ions required for its neutralisation and will remain in a free state:

$$Cl_2 + OH^- = HOCl + Cl^-. \qquad \text{(XVII-2)}$$

Hypochloric acid will then react with hypochlorite ions to form chlorate (in an intermediary stage chlorite is formed):

$$2\ HOCl + ClO^- = ClO_3^- + 2H^+ + 2Cl^-. \qquad \text{(XVII-3)}$$

The instantaneous rate r of this reaction expressed by the differential increase in the number of chlorate gram-ions $dn_{ClO_3^-}$ over a short interval of time dt in

unit volume V of the solution, or the differential change of the concentration of gram-ions of chlorate $dc_{ClO_3^-}$ over a short interval of time dt, depends on the instantaneous concentration of the reacting substances according to the equation:

$$r = \frac{dn_{ClO_3^-}}{V dt} = \frac{dc_{ClO_3^-}}{dt} = k c_{ClO^-} \cdot c^2_{HOCl}. \qquad \text{(XVII-4)}$$

From the above relation it is evident that the chlorate formation rate is proportional to the concentration of the hypochlorite ions c_{ClO^-}, but rises with the square of the hypochlorous acid concentration c_{HOCl}. In order to achieve a sufficiently high reaction rate, it is necessary to introduce surplus chlorine into the hydroxide, so as to ensure a high concentration of hypochlorous acid in the solution.

If a sufficient amount of free hypochlorous acid is present, chlorate will be formed even at a lower temperature, the reaction rate (XVII-3), however, will be far greater at a higher temperature, as the value of the reaction velocity constant k rises rapidly with temperature. If hypochlorite is to be quickly converted into chlorate the temperature during the second stage of chlorination must be therefore maintained at a sufficiently high level.

As it is evident from equation (XVII-3) the reaction of two moles of hypochlorous acid with hypochlorite results in formation of one gram-ion ClO_3^- apart from two moles of strong hydrochloric acid, which instantaneously decomposes further two moles of hypochlorite. So the slightly dissociated hypochlorous acid results:

$$2\ H^+ + 2ClO^- = 2\ HOCl. \qquad \text{(XVII-5)}$$

Regenerated hypochlorous acid reacts again with the hypochlorite according to equation (XVII-3), and the whole cycle starts being repeated again and again. It is clear from the reactions cited above that hydrochloric acid carries the oxygen from the hypochlorite to the chlorate until all the hypochlorite ions have disappeared.

If we add equations (XVII-3) and (XVII-5), we obtain an equation which expresses the process in the second stage of hydroxide chlorination:

$$3\ ClO^- = ClO_3^- + 2\ Cl^-. \qquad \text{(XVII-6)}$$

If this equation is combined with equation (XVII-1), an overall equation is obtained expressing the chemical formation of chlorates:

$$3\ Cl_2 + 6\ OH^- = ClO_3^- + 5\ Cl^- + 3\ H_2O. \qquad \text{(XVII-7)}$$

In order to avoid the use of expensive hydroxides of alkali metals, manufactured e. g. by the electrolysis, Liebig started from milk of lime and obtained calcium chlorate as an intermediary product, which was finally converted into potassium chlorate by potassium chloride.

Calcium chlorate is formed by absorption of chlorine in warm milk of lime according to the summary equation:

$$6\,Ca(OH)_2 + 6\,Cl_2 = Ca(ClO_3)_2 + 5\,CaCl_2 + 6\,H_2O. \qquad \text{(XVII-8)}$$

Absorption is carried out in a system of towers or tanks provided with mixers and cooling jackets, connected in series and arranged in cascades. Chlorine, introduced into the last tank, passes in countercurrent to the flow of the milk of lime (100 to 200 g. Ca O per 1.). In the first tank temperature is maintained at 30 °C, in the second at 40 to 50 °C, in the third at 60 to 70 °C, and in the last one at 35 to 40 °C. The final solution is filtered, concentrated in a vacuum evaporator, cooled and a certain amount of separated crystals of calcium chloride centrifuged. Into a clear, reheated solution surplus potassium chloride is added, in order to achieve the conversion:

$$Ca(ClO_3)_2 + 2\,KCl = CaCl_2 + 2\,KClO_3. \qquad \text{(XVII-9)}$$

After the solution is cooled, crystalline potassium chlorate is separated.

As far as the utilization of chlorine is concerned, Liebig's method is very uneconomic. As we can see from the equation (XVII-7), only one sixth of the chlorine introduced is utilized for the manufacture of chlorate, whilst the remaining five sixths are converted into almost worthless calcium chloride. Therefore this method is seldom used, as it cannot compete with the modern electrolytical method of manufacturing chlorate the production costs of which are only one third of the cost of the Liebig method.

B. THE ELECTROCHEMICAL MANUFACTURE OF CHLORATES

Sodium chlorate is produced by the electrolysis of a sodium chloride solution in an electrolyzer without a diaphragm, having an iron cathode and a magnetite or graphite anode. For the manufacture of potassium chlorate either the sodium chloride solution is used, or a mixed solution of both sodium and potassium chloride. The chlorate solution obtained will finally be converted with potassium chloride into potassium chlorate, which is separated by crystallisation while the mother liquor is returned to the electrolytic process. The potassium chloride solution will not be electrolyzed directly as potassium chlorate is sparingly soluble and the potassium chloride entrained in the chlorate crystals is not easy to remove.

1. Theoretical principles

a) *Processes at the cathode*

Because of the low hydrogen overvoltage iron is a suitable cathode material in the chlorate manufacture. The cathodic reaction proceeds according to the following equation:

$$2\,H_2O + 2e = 2\,OH^- + H_2. \qquad \text{(XVII-10)}$$

Because both the hypochlorite and the chlorate are reduced at the iron cathode, 5 to 10 g per litre of sodium or potassium chromate is added to the electrolyte, which suppresses the cathodic reduction to 1 to 3 per cent. Calcium or magnesium chloride will act in an analogous way.

b) *Processes at the anode*

α) Influence of hydrogen ion concentration

When describing the manufacture of hypochlorites, we have stated the conditions under which chlorates can be formed in the course of the electrolysis of neutral solutions of alkali chlorides. We have shown that smooth platinum is the most suitable anode material, ensuring with neutral solutions the highest yields of chlorate, i. e. 66.67 per cent. Under this condition the chlorate is almost exclusively formed by electrochemical oxidation:

$$6\,ClO^- + 6\,OH^- = 2\,ClO_3^- + 4\,Cl^- + 3/2\,O_2 + 3\,H_2O + 6e. \quad \text{(XVII-11)}$$

Also in an alkaline solution chlorate is the product of an electrochemical reaction. In this case hypochlorous acid formed by hydrolysis of the dissolved chlorine is neutralised in the immediate vicinity of the anode and the resulting hypochlorite ions are oxidized at the electrode to chlorate ions, as soon as formed (see equation (XVII-11)). Therefore, the concentration of hypochlorite ions in the bulk of the solution with an alkaline electrolyte will be lower than in a neutral one. The current efficiency in a slightly alkaline solution may reach 66.67 per cent, but it decreases with rising alkalinity as a result of increasing hydroxyl ions discharge. However, if current efficiency approximating 60 per cent, which was normal in the first plants for electrochemical manufacture of chlorates, is acceptable, work with a moderately alkaline electrolyte will be the easiest.

Generally a weak acid solution is preferred, in which only a small part of chlorate is formed by the electrochemical reaction (XVII-11), whilst the greater part is formed by the chemical reaction:

$$ClO^- + 2\,HOCl = ClO_3^- + 2\,H^+ + 2\,Cl^-. \quad \text{(XVII-12)}$$

The advantage of chlorate formation by the chemical reaction as compared to the electrochemical reaction is obvious, because the process (XVII-12) proceeds without oxygen losses, which is not the case with the reaction (XVII-11). It is, therefore, easy to understand that the more of the hypochlorite ions is converted to chlorate by the chemical reaction, the better is the current efficiency. In practice, however, the discharge of ClO^- ions cannot be eliminated entirely so that current efficiencies attain 75 to 95 per cent according to the electrodes used.

In the hypochlorite manufacture the reaction (XVII-12) is suppressed by operation with a neutral solution at a low temperature, but in chlorate production this reaction is deliberately promoted by acidifying the electrolyte and by raising the temperature. By adding a certain amount of hydrochloric acid, an

equivalent amount of hypochlorous acid is set free from the hypochlorite. This acid then oxidizes the remaining hypochlorite ions to chlorate ions, according to the equation (XVII-12). The H^+ ions set free react with further hypochlorite so that the process of chemical oxydation of hypochlorite ions is continually repeated in the whole volume of the electrolyte. The purpose of raising the temperature is to increase the reaction rate (by raising the temperature from 20 °C to 80 °C the rate of the reaction (XVII-12) is increased almost a hundred times).

After the electrolyte has been acidified, a new stationary concentration of ClO^- ions is established which, however, compared to neutral solution is far lower. Also the current efficiency reaches a stationary value; within a unit of time as many hypochlorite ions will be formed as necessary for both the electrochemical and the chemical formation of chlorate ions.

When raising the concentration of the hydrogen ions in the electrolyte care must be taken as a high admixture of hydrochloric acid may cause the following reaction to take place:

$$HCl + HOCl = Cl_2 + H_2O, \qquad \text{(XVII-13)}$$

which would cause a loss in active chlorine.

The best results are obtained if two thirds of the total hypochlorite content is present in the form of free acid, which corresponds to a concentration of hydrogen ions in the solution pH = 6 to 7 according to the sodium chloride concentration in the brine and according to temperature. Because a small amount of chlorine escapes into the ambient atmosphere, hydrochloric acid must be gradually added in small quantities to the electrolyte during the process.

The admixture of acid causes the CrO_4^{--} ions from the added chromate to be converted into bichromate ions $Cr_2O_7^{--}$, which give the electrolyte an orange colour:

$$2\ CrO_4^{--} + 2\ H^+ = Cr_2O_7^{--} + H_2O. \qquad \text{(XVII-14)}$$

If the acidity of the electrolyte is insufficient, hypochlorite will reconvert the $Cr_2O_7^{--}$ ions into CrO_4^{--} ions, the latter will give the electrolyte a yellow colour:

$$Cr_2O_7^{--} + 2\ ClO^- + H_2O = 2\ CrO_4^{--} + 2\ HOCl. \qquad \text{(XVII-15)}$$

It appears from the above equations that apart from its main role which is to restrict the cathodic reduction, chromate will also act as an automatic acidity buffer. With an increased acidity the equilibrium (XVII-14) is shifted to the right and the hydrogen ions are fixed; with a decreased acidity the reaction (XVII-15) will, on the contrary, supply the required amount of hypochlorous acid.

β) Influence of current concentration

As is apparent from equation (XVII-4), the increase in gram-ions of chlorate d $(n_{ClO_3^-})_{chem}$, formed by the chemical oxidation of hypochlorite within a very

short interval of time dt, is defined by the product of the instantaneous reaction rate r and the volume of the solution V, then $d(n_{ClO_3^-})_{chem}/dt = rV$. On the other hand, the increase in the number of ClO_3^- gram-ions, formed during the same time by electrochemical oxidation, is directly proportional to the current passing through the electrolyzer, then $d(n_{ClO_3^-})_{el}/dt = KI$. From the quotient of the two differential expressions it follows that the ratio of the number of chlorate gram-ions formed by electrochemical oxidation to the number of chlorate gram-ions formed by chemical reaction will be lower, the lower the value of the fraction I/V. The fraction I/V is called the current concentration and is expressed in amperes per one litre of electrolyte. At a low current concentration a major part of the hypochlorite will, therefore, be oxidized to chlorate by the chemical reaction, and only a slight part by electrochemical one; so the current efficiency will increase. A low current concentration can be achieved if an electrolytic tank is used in which the liquid level is much higher than the upper ends of the electrodes. Such an arrangement will also assist in the complete absorption of the chlorine.

γ) Influence of the electrode material

An acid brine electrolysis will give the best results if smooth platinum anodes are used. If chromate is added and the electrolyte temperature is maintained at 75 to 80 °C, a current efficiency of 95 per cent can be obtained. Nowadays, graphite or magnetite is substituted for platinum.

Graphite electrodes have a drawback, as the lower oxygen overvoltage will facilitate a simultaneous discharge of the hydroxyl ions together with the chloride ions, particularly in the graphite pores, which causes the electrodes to rapidly disintegrate. In order to reduce these undesirable consequences the electrolysis temperature must be kept below 40 to 50 °C. Moreover, a somewhat more acid electrolyte (some 40 milli-equivalents HCl per litre) must be used with graphite electrodes than with platinum or magnetite electrodes, in order to raise the discharge potential of the hydroxyl ions. Nevertheless, all these measures are not entirely successful, so that current efficiency varies between 75 and 85 per cent, and is always inferior to the figures attained with platinum. Under normal operating conditions with a current density of 2.7 A per sq. dm, the average cell voltage reaches 3.3 V.

The advantage of the magnetite electrodes lies in the fact that it is possible to electrolyse at an elevated temperature of 70 to 80 °C, which considerably accelerates the chemical oxidation of hypochlorite, and so indirectly increases the current efficiency. However, magnetite electrodes are brittle, their electrical conductivity is low and they do not permit to use current density which exceeds 2 to 3 A per sq. dm. Magnetite electrodes are either in the form of hollow bars or tiles, which are closed at the bottom and electroplated inside with copper. Copper increases the conductivity of the electrode and enables current conductors to be soldered to the top of it without any difficulty. The current efficiency obtained with magnetite electrodes reaches 86 to 90 p. c., and

is higher than that obtained with graphite. On the other hand, the high chlorine overvoltage on magnetite causes the cell voltage to be higher (i. e. 3.6 to 3.8 V).

c) *Energy consumption*

Electrochemical oxidation of one gram-ion Cl^- to ClO_3^- requires $6 \cdot 26.82 = 160.9$ A-hr. The theoretical quantity of electricity needed to produce 1 kg of potassium chlorate is 1313 A-hr. The production of 1 kg of sodium chlorate requires 1512 A-hr.

The theoretical voltage needed for electrochemical decomposition of chloride under the simultaneous formation of chlorate is calculated in the same way as has been used for hypochlorites. In a neutral solution ($a_{OH^-} = 10^{-7}$) at a hydrogen pressure of $p_{H_2} = 1$ atm., the reduction potential at the cathode where reaction (XVII-10) occurs, will equal

$$\pi_{OH^- \mid H_2, Pt} = -0.414 \text{ V}. \qquad \text{(XVII-16)}$$

During the electrochemical oxidation of chloride, chlorate is formed in accordance with the equation:

$$Cl^- + 6\ OH^- = ClO_3^- + 3\ H_2O + 6e. \qquad \text{(XVII-17)}$$

The standard potential of this reaction equals $\varepsilon^\circ_{Pt, \mid Cl^-, ClO_3^-} = -0.62$ V. If we assume that the solution is neutral, and the activity a of both chloride and chlorate ions is unity, the following equation is valid at 25 °C according to Nernst's law:

$$\varepsilon_{Pt \mid Cl^-, ClO_3^-} = \varepsilon^\circ_{Pt \mid Cl^-, ClO_3^-} - \frac{RT}{6F} \ln \frac{a_{ClO_3^-}}{a_{Cl^-} a^6_{OH}} \qquad \text{(XVII-18)}$$

$$= -0.62 + 0.05915 \log 10^{-7} = -1.034 \text{ V}.$$

By adding the values (XVII-16 and XVII-18), the resulting theoretical decomposition voltage can be ascertained:

$$(E_R)_t = -E'_{min} = -(\pi_{OH^- \mid H_2, Pt} + \varepsilon_{Pt \mid Cl^-, ClO_3^-}) = 1.448 \text{ V}. \qquad \text{(XVII-19)}$$

A comparision of this value with the decomposition voltage required for the hypochlorite manufacture, equalling 1.768 V, shows that the former is somewhat lower, which agrees with the fact that chlorate is a more stable product of electrolysis than hypochlorite.

2. The manufacture of sodium chlorate

The equipment here described consists of electrolyzers having magnetite electrodes and operating at a temperature of 70 °C.

Rock salt as well as salt recovered by evaporation of the electrolyte is dissolved at 60 °C, in the mother liquor from the previous operation. Iron tanks provided with stirrers and steam coils are used for dissolution. Soda is added to the solution to precipitate calcium ions. Otherwise, the calcium ions would

hinder the subsequent electrolysis, as they would be deposited on the cathodes as a sediment. Also the required amount of sodium chromate is added to the electrolyte. Brine is introduced to settling tanks, where impurities separate, and is then passed through sand filters; finally hydrochloric acid is added. The electrolyte so treated is then led into the electrolyzer. It contains the following quantities per litre: 270 to 280 g NaCl, 50 to 60 g $NaClO_3$, 12 to 14 g Na_2SO_4 and some 5 g $Na_2Cr_2O_7$. Its acidity corresponds to 0.016 N-HCl.

The electrolysis is carried out in a set of steel tanks arranged in cascades (for a 9000 to 12 000 A load the tank measures 3 000 . 2 000 . 1 400 mm). They are lined with acid resisting bricks. Suspended in each tank are 144 anodes and 28 steel sheets acting as cathodes arranged in parallel rows. The magnetite electrodes shaped as narrow, hollow tiles closed at the bottom (120 . 50 . . 1 200 mm) are electroplated inside with copper. The cathodes which surround the anode rows from both sides are made of perforated iron sheets. The purpose of the perforation is to enable the stirring of the electrolyte by the escaping hydrogen bubbles and also to increase the current density at the cathode which suppresses the reduction of the hypochlorite and chlorate ions. At a 12 000 A load the current density reaches 2.5 A per sq. dm at the anodes and 3 A per sq. dm at the cathodes The distance between anodes and cathodes is 20 mm. In order to achieve a low current concentration of 2 A per litre, large free space is left for the electrolyte either above the electrodes or between them.

All electrodes are suspended from a cement or asbestos-cement cover, which closes tightly the tank. Generally, a coil is fixed in the middle of the tank, through which cooling water passes in order to maintain the desired temperature. The coil is conductively connected with the cathodes to prevent corrosion. Hydrogen evolved at the cathode passes through a pipe at the cover. Hydrochloric acid is continuously introduced into the electrolyte by another pipe in the cover, in quantities sufficient to maintain the acidity of the solution at 0.016 N-HCl. The electrolyzers are equipped with convenient overflows, through which the electrolyte flows to the tank below. Each tank holds about 5.5 cu. m of electrolyte, which is maintained at 70 °C.

In the lowest tank of the cascade, which has no electrodes, the remaining hypochlorite is removed from the liquor, because otherwise the hypochlorite may corrode the steel parts of the next equipment. For this purpose the electrolyte in the lowest tank is heated to 80 to 95 °C, to convert hypochlorite into chlorate. The remaining traces of hypochlorite are reduced by formic acid. Finally, the electrolyte is neutralized by sodium hydroxide, to precipitate iron which passed into the solution from the cathodes.

The resultant electrolyte is now slightly alkaline and contains the following amounts of substances per litre: 280 to 300 g of $NaClO_3$, 160 to 180 g of NaCl and 6 g of Na_2CrO_4. This liquor first passes through a sand filter and is then evaporated in a double-effect vacuum evaporator to a density about 1.6. During evaporation, sodium chloride crystallizes, is separated in a suction filter and returned to the preparation of brine.

The concentrated solution (which contains per litre 900 g of $NaClO_3$, 80 to 90 g of NaCl and 18 g of Na_2CrO_4), is pumped into a vessel provided with a stirrer and a steam coil, where, at 100 °C, the second-grade chlorate is dissolved. This chlorate is obtained at a later stage of the manufacturing process. The solution which now contains 1 050 to 1 100 g of $NaClO_3$ per litre and has a density 1.63, is again filtered through sand and introduced into vacuum crystallizers where it is cooled to 40 °C. Sodium chlorate crystals separated by cooling are filtered off in suction filters provided with a metallic cloth, and finally centrifuged. The crystals are then dried under reduced pressure (some 500 mm Hg) at 90 °C in a Passburg vacuum dryer equipped with a heating jacket and a stirring device. The dried product falls from the dryer directly into sheet metal drums. A second grade product is obtained by evaporating and cooling the mother liquor that has passed through the suction filter already mentioned. The crystals of the second grade product are returned into the process and dissolved as described above. After the crystals have been separated, the mother liquor is returned for the dissolution of salt (preparation of fresh brine).

Works which do not have cheap steam at their disposal will find it more economical to separate the chlorate from the solution by cooling at a sufficiently low temperature. In such a case the solution to be prepared by electrolysis must have as high a sodium chlorate content as possible (containing some 500 g of $NaClO_3$ and 150 g of NaCl per litre). After the remaining hypochlorous acid has been decomposed by heating and stirring and the impurities separated by sedimentation, the solution is cooled to — 5 °C, in a crystallizer in the cooling system of which liquid ammonia is evaporated. The separated crystals are centrifuged and dried in a vacuum dryer, whilst the mother liquor is returned to the process.

The final product is usually yellowish-gray and contains 0.3 per cent NaCl. A pure product is obtained by recrystallisation. It contains mo more than 0.05 per cent sodium chloride. With an average voltage of 3.8 V and an average current efficiency of 88 per cent, the energy consumption will be approximately 650 kw.-hr. per 100 kgs. of product.

Hydrogen escaping from electrolyzers in a plant that operates properly contains 3—5 % oxygen and 0.5—2 % chlorine. Sometimes this can be further utilized. In this event the gas is first scrubbed in towers with a caustic soda solution to remove the chlorine, then it passes into the catalytic chambers, where, at 500 °C the oxygen is removed on a catalyst consisting of platinum dispersed on a suitable carrier. The hot purified hydrogen is cooled by spraying with water, then dried and delivered to where required.

3. The manufacture of potassium chlorate

Electrolysis in this case only differs slightly from the sodium chlorate process. A sodium chloride solution or a mixed solution of sodium and potassium chloride is used as the electrolyte. The sodium chlorate in the electrolytically treated brine is converted to potassium salt by double decomposition with potassium

chloride. After cooling potassium chlorate crystallizes out and is separated by filtration. The mother liquor is recycled after being acidified.

If a mixed chloride solution is used, the electrolyte contains 70 to 100 g $KClO_3$, 180 to 220 g NaCl, 100 to 130 g KCl, 4 to 6 g $Na_2Cr_2O_7$ and 20 milli-equivalents HCl per litre when electrolysis commences. After passing through the cascade, it is neutralized with caustic. Now it contains 150 to 200 g $KClO_3$, 80 to 120 g $NaClO_3$, 50 to 70 g KCl, 140 to 160 g NaCl and about 5 g $Na_2Cr_2O_7$ per litre. The solution leaving the electrolyzer is first heated to 90—100 °C and then pumped into a conversion vessel, provided with a stirrer and a steam coil. Solid potassium chloride is added to the solution in the vessel by which sodium chlorate is converted into potassium chlorate. The solution which now contains 270 to 300 g $KClO_3$, 180 to 200 g NaCl, 100 to 130 g KCl and some 6 g Na_2CrO_4, is cooled to 35—40 °C in vacuum crystallizers and separated crystals of raw potassium chlorate are filtered off in a suction filter and washed. Afterwards, the mother liquor will be resaturated so as to correspond to the solution entering electrolysis. Calcium salts, brought into the solution by the potassium chloride, are then precipitated with the addition of soda ash. The decanted mother liquor will be filtered through a layer of sand, and after being acidified with hypochloric acid, returned for electrochemical oxidation.

After the raw chlorate has been washed, the wash water, which is rich in sodium chloride, is boiled down in an evaporator and the common salt precipitated is separated in a suction filter and reused. In this way, a portion of the sodium chloride is removed from the electrolytic liquor. Failing this the content of NaCl would continually increase, as the potassium chloride used always contains some sodium salt. Hot mother liquor is cooled in a vacuum cooler, where further portions of potassium chlorate are crystallized.

Crude potassium chlorate is again purified by recrystallisation. It is dissolved in the boiling mother liquor remaining after the previous crystallisation of pure chlorate. If the crude product contains potassium bromate which cannot be removed by recrystallisation (because the $KBrO_3$ crystals are isomorphous with $KClO_3$) sodium sulphide must be added to the solution. This reduces the bromate to bromide and is simultaneously oxidized into sulphate. The hot solution is then filtered and cooled in a vacuum cooler. Precipitated crystals are then separated in a suction filter, washed with water and dried in a vacuum dryer. The dry product is eventually ground into a fine powder, packed in wooden barrels lined with paper and spread over with water-glass. The final product contains 99.8 to 99.9 per cent $KClO_3$, 0.01 to 0.03 per cent KCl, not more than 0.1 per cent $KBrO_3$ and not more than 0.05 per cent H_2O. About 570 kw-hr are required to manufacture 100 kg of chlorate.

C. USES OF CHLORATES

Sodium chlorate is used for oxidation in organic industries and for the manufacture of perchlorates. Very often it is used as a 2 per cent solution, to destroy

weeds on railway-tracks and garden paths. For the same purpose also a solution of calcium chlorate is sometimes used containing 33 per cent $Ca(ClO_3)_2$ and 20 per cent $CaCl_2$. This is produced by introducing chlorine into milk of lime, and separating the excessive calcium chloride after the solution has been chilled or evaporated.

Potassium chlorate is used as an oxidizing agent in vat dyeing, for printed calico, for pyrotechnical purposes but mainly in the manufacture of matches. For pharmaceutical use, the so called "santonine" form of fine, scale shaped crystals is sometimes demanded. These are formed by the saturated solutions when they are slowly cooled.

In Czechoslovakia, various grades of chlorate are manufactured as per technical specifications indicated in Table 18.

Table 18. Sodium chlorate

	Purum "p. a." %	Depuratum "pure" %	Technical product %
$NaClO_3$, min.	99	99	99,7
Water insoluble substances, max.	0,01	0,02	0,05
Cl^-, max.	0,005	0,02	0,06
SO_4^{--}, max.	0,003	0,01	0,03
BrO_3^-, max.	0,07	0,07	—
Heavy metals, max.	0,001	0,002	—
Fe, max.	0,0005	0,002	—

Technical potassium chlorate

	%
$KClO_3$, min.	99,7
Water insoluble substances, max.	0,05
KCl, max.	0,05
Sulphates computed as $CaSO_4$, max.	0,05
Heavy metals, max.	0,005
Fe, max.	0,005
$KBrO_3$, max.	0,05

XVIII. PERCHLORATES

Perchlorates are most stable of all the salts of oxy-acids of chlorine. Potassium perchlorate is commercially the most important salt of perchloric acid. This salt is a colourless powder having the formula $KClO_4$, only sparingly soluble in water. If heated to high temperatures, it liberates oxygen.

A. CHEMICAL MANUFACTURE OF PERCHLORATES

Perchlorates can be manufactured on a small scale through decomposing the chlorates by careful heating in a quartz or porcelain crucible. Thus, e. g. potassium chlorate, if heated to 450 to 510 °C will be converted into perchlorate according to the following equation:

$$4\ KClO_3 = 3\ KClO_4 + KCl. \qquad \text{(XVIII-1)}$$

At the same time a small amount of chlorate is decomposed into chloride and oxygen:

$$2\ KClO_3 = 2\ KCl + 3\ O_2. \qquad \text{(XVIII-2)}$$

When heated, the substance first melts, then turns into a paste, and finally solidifies. At higher temperatures or when heated excessively, the perchlorate decomposes further into potassium chloride and oxygen:

$$KClO_4 = KCl + 2\ O_2. \qquad \text{(XVIII-3)}$$

For this reason the time of heating must be watched carefully. After the reaction mass has cooled it is leached with cold water in order to separate the easily soluble potassium chloride from the sparingly soluble potassium perchlorate. Eventually the potassium perchlorate is recrystallized from a hot water solution. The described method is commercialy unimportant as one quarter of the chlorate at least is converted into worthless potassium chloride (see equation XVIII-1).

B. ELECTROCHEMICAL MANUFACTURE OF PERCHLORATES

Manufacture of different metal perchlorates starts from sodium perchlorate which is, because of its high solubility, easy to prepare electrochemically. Sodium perchlorate is, however, not much used commercially, as it is deliquescent, yet it is an intermediary product for the manufacture of other perchlorates.

Sodium perchlorate is prepared by electrolysis of concentrated solutions of sodium chlorate in cells without diaphragms using platinum anodes and iron cathodes. Electrolysis is continued until some 95 per cent of the initial chlorate

is converted into perchlorate. In order to reach a satisfactory current efficiency, the operation is performed at a high anode current density and with the addition of hydrochloric acid and a chromate. The temperature of the electrolyte is kept at 35 °C.

1. Theoretical principles

At the anode ClO_3^- ions are primarily discharged and chloric acid and oxygen are formed according to equation:

$$2\ ClO_3^- + H_2O = 2\ HClO_3 + 1/2\ O_2 + 2e. \qquad \text{(XVIII-4)}$$

However, chloric acid is not stable and decomposes partly into chlorous and perchloric acids:

$$2\ HClO_3 = HClO_2 + HClO_4. \qquad \text{(XVIII-5)}$$

The oxygen evolved at the anode rapidly oxidizes the arising chlorous acid into chloric acid so that the overall reaction at the anode may be expressed by the equation:

$$2\ ClO_3^- + H_2O = HClO_4 + HClO_3 + 2e. \qquad \text{(XVIII-6)}$$

Hydrogen is discharged at the cathode and leaves hydroxyl ions in the electrolyte:

$$2\ H_2O + 2e = H_2 + 2\ OH^-, \qquad \text{(XVIII-7)}$$

so that chloric and perchloric acids arising in accordance with eqation XVIII-6 are neutralized. The total process occurring in the electrolyzer can be expressed by the following equation:

$$ClO_3^- + H_2O = ClO_4^- + H_2. \qquad \text{(XVIII-8)}$$

This main process is also accompanied by secondary reactions resulting in the discharge of ClO_3^- and ClO^- ions; in both instances oxygen will be evolved.

The first side reaction is induced by an elevated temperature, because due to the lowering of the oxygen overvoltage at the platinum anode the oxidation of the ClO_3^- ions already ceases in the first stage, which is expressed by the equation (XVIII-4). The unfavourable influence of a higher temperature can be offset to a considerable extent if a higher anode current density is used. Thus, e. g. if densities exceeding 30 A per sq. dm are used, no oxygen is evolved even if the temperature rises up to 60 °C.

The second side reaction is caused by chloride ions, which, although not present in the initial electrolyte, arise during electrolysis from the reduction of chlorate at the cathode.

These ions are undesirable because they are oxidized to ClO^- and further to ClO_3^- ions rather than the ClO_3^- to ClO_4^- ions. In order to restrict secondary oxidation at the anode as much as possible, sodium chromate is added to the electrolyte to prevent the chlorate being reduced at the cathode. Besides this,

the electrolyte is slightly acidified, the temperature is not allowed to fall below 30 °C and a low current concentration is used. All these measures promote the chemical oxidation of ClO^- ions to ClO_3^-, as explained in the chapter dealing with the manufacture of chlorates. A higher temperature accelerates the reaction between the hypochlorite ions and the hypochlorous acid, but it has an unfavourable influence on the evolution of oxygen according to reaction (XVIII-4). This effect can be compensated by an adequate increase in current density at the anode.

The process is discontinued when some 95 per cent of the chlorate has been converted into perchlorate. Electrolysis beyond this limit would entail a sudden drop in the current efficiency and oxygen would be evolved at the anode.

After the electrolysis has been finished, solid sodium perchlorate may be separated from the solution, but usually other salts of perchloric acid are the final products, which are more suitable for commercial use. Potassium perchlorate is prepared by double decomposition of sodium perchlorate solution with potassium chloride. If ammonium chloride or sulphate is used for the conversion, ammonium perchlorate will be obtained. Similarly, a mutual reaction with barium chloride will result in barium perchlorate.

Iron is the usual material for cathodes operating at a current density between 10 to 20 A per sq. dm. Graphite or nickel is rarely used. Smooth platinum is the only suitable material for anodes as it has a sufficiently high oxygen overvoltage and so enables a high current density, of between 30 to 60 A per sq. dm, to be employed.

2. Industrial manufacture of perchlorates

The design of electrolyzers used for the manufacture of perchlorates does not substantially differ from those used for the manufacture of chlorates. The steel tank which is constructed for 12 000 A is 3 000 mm long, 2 100 mm wide and 1 400 mm high. It is provided with a cover and a vent pipe through which the gases containing a small amount of ozone are drawn off by means of a fan. 15 anodes made of platinum foil measuring 550 × 220 mm and 0.05 mm thick are suspended in the electrolyzer. The foil is fastened to a copper frame into which the current is led from above. The frame is covered with a polyvinylchloride or hard rubber coating to prevent corrosion.

The cathodes, totalling 32 elements and measuring 680 × 250 × 3 mm are made of perforated MS sheet. Each anode is placed between two cathodes at a spacing of 10 mm. The electrodes are kept apart by means of small glass rods. Apart from this six cathodically polarized coils, through which the cooling water passes, are inserted in the tank.

At a normal current load of the bath, i. e. at 12 000 A, at an anode current density of 30 A per sq. dm., and at an operating temperature of 35 °C, the voltage across the cell amounts to 6.5 V. The current efficiency equals some 85 per cent.

Electrolysis is carried out in series of tanks arranged in cascades. The initial solution is slightly acidified by hydrochloric acid and contains per litre 400 to 500 g sodium chlorate and 3 to 5 g sodium bichromate. The solution after flowing through the cascade is resaturated by chlorate and pumped again into the highest electrolyzer. It is recirculated until it contains per litre some 1 000 g of perchlorate and less than 50 g of chlorate.

If sodium perchlorate should be manufactured the final solution from the electrolysis is neutralized with soda and boiled down in an evaporator until it contains about 1 300 g $NaClO_4$ per litre. The concentrated liquid is filtered and the salt allowed to crystallize by cooling to 30 °C in aluminium crystallizers. Precipitated crystals of sodium perchlorate are separated from the mother liquor in aluminium suction filters, washed with water, centrifuged, dried with hot air and finally ground to powder.

As already stated potassium salt is more frequently prepared than sodium perchlorate. In this event the sodium perchlorate solution on leaving the electrolysis after being neutralized with soda will be pumped into a vacuum crystallizer, into which hot potassium chloride solution (300 g KCl per l.) is added. The conversion is an exothermic reaction and the temperature of the solution in the crystallizer will rise to 90—100 °C. By gradually reducing the pressure in the crystallizer to 30 to 40 mm Hg, the solution is cooled to 35 to 40 °C and potassium perchlorate is crystallized. This crystalline mass is filtered off and washed. The first mother liquor containing per litre some 70 g $KClO_4$ and 190 g NaCl is evaporated, which will cause first sodium chloride to crystallize. It is separated and used again for the manufacture of chlorate. The second mother liquor is cooled in a vacuum crystallizer, and separated crystals of $KClO_4$ are filtered off. The two products are now combined, recrystallized, dried and finally ground to powder. All the remaining liquors are partly utilized to wash the individual crystal fractions and partly recirculated to prepare the fresh electrolyte. 300 to 320 kw-hr. are required to manufacture 100 kg of potassium perchlorate.

The final product generally contains 0.04 to 0.1 per cent $KClO_3$ and not more than 0.02 per cent KCl. Potassium perchlorate is used for the manufacture of explosives and in pyrotechnics as well as for the manufacture of perchloric acid.

In the manufacture of explosives ammonium perchlorate has a similar importance. Magnesium salt $Mg(ClO_4)_2 . 7 H_2O$ can be dehydrated comparatively easily and the anhydrous salt is used for drying gases in place of phosphorus pentoxide. If the substance becomes humid during the drying operation, it can be dehydrated and re-used. The salt is prepared through dissolving magnesium oxide in perchloric acid. Barium and strontium perchlorates are used in the manufacture of fireworks and flares.

XIX. FLUORINE

Fluorine is a pale yellowish-green gas. It is very harmful to the human body. One litre of fluorine weighs 1.695 g (under normal conditions). By intensive cooling it can be liquefied to give a clear yellow liquid, the boiling point of which is — 188 °C. When cooled in a bath of boiling liquid hydrogen it solidifies to a substance which is yellow at first and becomes finally colourless; its melting point is — 218 °C. The critical temperature of fluorine is — 129 °C, and the critical pressure equals 55 atm. Fluorine is the most electronegative element; its oxidation potential is — 2.85 V.

Fluorine is an extremely reactive element, which combines directly or indirectly with nearly all substances. Reactions with elementar fluorine are very violent and sometimes explosions occur so that extreme care must be taken. As the deposition potential of fluorine greatly exceeds the deposition potentials of all other substances, it can be only prepared by electrolysis of its compounds. Due to the fact that water is decomposed by fluorine electrolysis must be effected in an anhydrous medium. Since the days of Moissan who first succeeded in isolating free fluorine, anhydrous hydrofluoric acid is used to prepare it. The electrical conductivity of this substance is very small and must be increased by the addition of alkali fluorides.

When constructing electrolyzers for this process it is rather difficult to find suitable materials which can resist the effects of fluorine as it attacks most metals even at normal temperature; fortunately continuous fluoride coatings are formed on the surface of some metals which protects them against further corrosion at least to a certain extent. Such metals are iron, nickel, Monel metal, aluminium and its alloys, magnesium and especially electron one of its alloys. However, the protective films are only stable at lower temperatures. At elevated temperatures a violent reaction proceeds between the fluorine and the metal. Monel metal and copper have relatively the best resistance against fluorine at elevated temperatures. These metals, therefore, were widely used to construct electrolyzers. In more recent designs, copper was replaced by steel or electron.

Platinum is not a suitable material for anodes, because it is considerably attacked by electrolytes used. Nickel is also subject to intensive corrosion, especially if the process is carried out at elevated temperatures. Copper has proved more advantageous; it is relatively suitable for electrolyzers operated at lower temperatures, about 100 °C. Nowadays graphite or special hard carbon are generally used for anodes according to the nature of the electrolyte.

Cathodes are usually made of copper, nickel, Monel metall, electron, graphite, steel or silver. They are either perforated or made of gauze to permit an effective circulation of the electrolyte. Diaphragms, too, are made of copper, iron, electron or Monel metal. They are necessary to prevent the gases from mixing and

causing an explosion (hydrogen and fluorine form highly explosive mixtures).

It is difficult to achieve a gas-tight seal to the anode current connections, which must also be electrically insulated against the cover of the electrolyzer, to which the cathodes are attached. Formerly, fused calcium fluoride was used as sealing material. This is, however, brittle and sometimes even porous; recently sintered corundum has been used and for the external packing teflone (polymerized tetrafluoro-ethylene), buna, and polyvinylchloride.

According to Moissan's method fluorine was produced by the electrolysis of anhydrous hydrofluoric acid. In order to increase its conductivity a comparatively small amount of potassium fluoride was added (about one mole of KF to 12 moles of HF). Due to the high vapour pressure of hydrogen fluoride over such a solution it was necessary to work at low temperatures (— 30 to — 50 °C), which was a considerable disadvantage.

Since 1920, the problem of large-scale production of fluorine has received increased attention. A number of different types of electrolyzers have been tried out, from small units taking 6 to 30 A to large-scale production units which are built for 1,500 to 4,000 A. All these electrolyzers may be divided into two main groups, according to the composition of the electrolyte used, and operating temperature. The first group consists of cells using potassium hydrogen fluoride KF . HF, which melts at 235 °C; such units operate at a temperature between 250 and 300 °C. The other group comprises cells using acid potassium fluoride of approximate composition KF . 2.5 HF to KF . 2 HF, which makes it possible to work at a temperature between 70 and 110 °C.

A. CELLS OPERATING AT A TEMPERATURE BETWEEN 250 AND 300 °C

The *Falkenhagen cell* is a design in which a melt of approximate composition KF . HF is electrolyzed at a temperature of 250 to 300 °C. The electrolyzer is designed for 2 000 A. It is made of electron and encased in an outer box of duralumin. The dimensions are 1 000 × 1 500 × 1 300 mm (see Fig. 134).

In the free space between the inner vessel and the outer box, resistance wires are placed to heat the electrolyzer at the start of the process. After the electrolyte has reached a sufficient temperature the electrical heating is disconnected and air, heated to some 230—250 °C, is blown into the space to keep a constant temperature in the bath during the electrolysis. 6 graphite anodes and 7 cathodes made of perforated silver sheet are alternately suspended in the inner vessel. Both cathodes and anodes are inserted into special diaphragms made of electron and perforated at the bottom. They enclose in the form of bells each electrode. The gases liberated during electrolysis are taken off at the top of the bells. The whole assembly of anodes and cathodes is covered by an electron cover.

Before the operation commences, the electrolyzer is filled with pure molten potassium hydrogen fluoride which has previously been completely dehydrated

by preliminary electrolysis in an electrolyzer similar to the one just described. There is only one difference, and that is the diaphragms are not fitted with collecting bells and the gas, after being diluted with air, is led into an absorber filled with sodium chloride. It then passes over activated charcoal and is

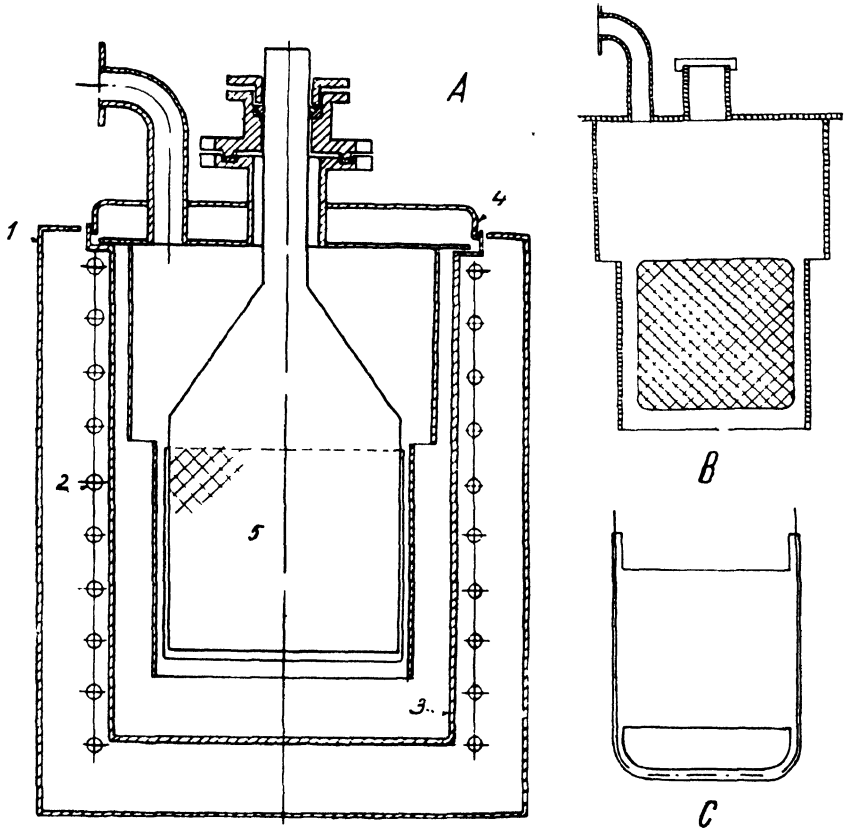


Fig. 134. Electrolyzer of Falkenhagen design for the preparation of fluorine.
A — Cross section of the electrolyzer, *1* — Outer box of the electrolyzer with electrical heating and circulation of hot air, *2* — Electric heating elements, *3* — Electrolyzer vessel, *4* — Electrolyzer cover, *5* — Graphite anode, *B* — Electron diaphragm, *C* — Cathode of perforated silver plate, some 1.5 mm thick, fixed to silver frame.

allowed to escape into the atmosphere. It is important to use dry potassium hydrogen fluoride because any moisture in the electrolyte considerably increases the polarization voltage at the anode and, moreover, oxygen rapidly attacks the graphite electrode.

The normal operating voltage across an electrolyzer taking 2 000 A equals 6.5 to 8 V, it increases, however, with time because of polarization, due to

a change in physical properties of the anode surface or to the formation of CF_4 and C_nF_{2n+2}. As soon as the voltage reaches 11.5 V a current of 5 000 A is allowed to flow at 60 V through the electrolyzer for 2 to 3 minutes; hereby the anode will be depolarized. If this measure is insufficient, it is necessary to remove the anode and to scrape off the surface; after this the voltage will drop to its normal value.

The gas escaping at the anode contains about 99 % F_2 after the hydrogen fluoride has been condensed by cooling; the remainder consists of oxygen, carbon dioxide, silicon tetrafluoride and carbon fluorides. At an anode current density of 10 A per sq. dm current efficiency equals 95 to 99 per cent. The output of one cell is on the average 1 kg of fluorine per hour. The electrolyte content lasts about one year and then it must be replaced.

During electrolysis the hydrogen fluoride is decomposed into fluorine and hydrogen, the latter being liberated at the cathode. To prevent any variation in the composition of the electrolyte a stream of pure hydrogen fluoride (prepared by the vaporization of distilled anhydrous liquid hydrogen fluoride) is lead under each cathode diaphragm by a special distributor and pipe. Before the gas is used in the electrolyzer, it is purified together with a small amount of fluorine by passing through a nickel pipe which is heated to 200—300 °C.

B. CELLS OPERATING AT A TEMPERATURE BETWEEN 80 AND 100 °C

During the war the firm of *I. G. Farben*, Leverkusen, developed an electrolyzer in which acid potassium fluoride of an approximate composition KF . 2.5 HF was used as an electrolyte. The cell made of electron is 3 000 mm long,

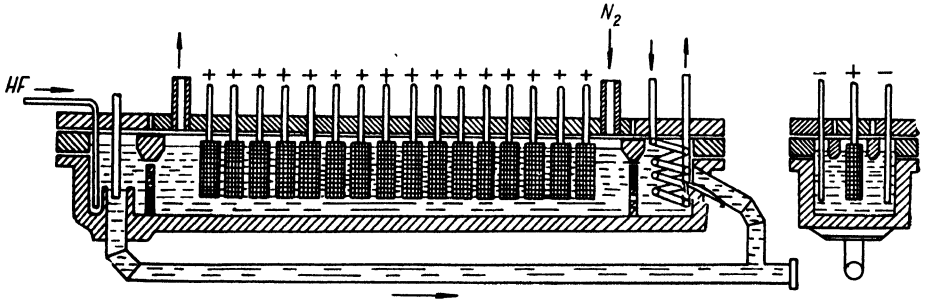


Fig. 135. Electrolyzer of I. G. Farben (Leverkusen) for the preparation of fluorine.

310 mm wide and 300 mm high (see Fig. 135). A row of 15 carbon anodes (120 × 50 × 350 mm) is suspended along the longitudinal axis between two rows of five cathodes made of electron sheet (height 350 mm, width 5 mm, total length 2 500 mm). The anodes are made of very hard carbon, with low

ash content and free of graphite, because the latter easily disintegrates if electrolyte with a high content of hydrofluoric acid is used. The liberated hydrogen and fluorine are separated by two electron barriers bolted to the cover, which only partially dip into the electrolyte between the cathodes and the anodes.

Electrolysis is carried out at a temperature of 70 to 75° C which is maintained by a suitable cooling of the electrolyte. This is done by allowing the electrolyte to circulate through an annular space between the outer electron pipe and an inner nickel pipe through which water flows. The circulation is actuated by a propeller revolving near the opening which connects the electrolyzer to the outer tube. At the other end of the vessel where the electrolyte returns to the electrolyzer, a nickel cooler is suspended, which helps the melt to cool and maintains the desired temperature.

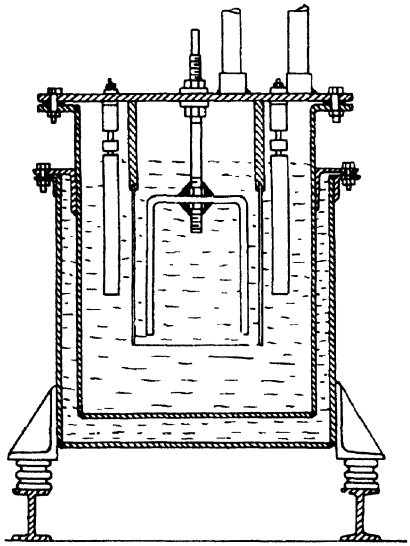


Fig. 136. Harshaw's electrolyzer for the preparation of fluorine.

The electrolyte is prepared in a vessel made of electron, filled with potassium fluoride, into which a calculated amount of gaseous hydrogen fluoride is introduced. The reaction liberates sufficient heat to melt the salt. The molten mass is then poured into the electrolyzer; in order to maintain a constant composition of the electrolyte during electrolysis, a stream of gaseous hydrogen fluoride is introduced in the vicinity of the actuating propeller. The hydrogen fluoride is prepared from non-distilled hydrofluoric acid and may contain up to 3 per cent of moisture and 1 per cent of silicofluoric acid.

A mixture of approximate composition KF . 2.5 HF which melts at 65 °C is advantageous, because its melting point does not vary very much within the range of composition from KF . 2 HF to KF . 3 HF. The voltage across the bath equals 11 to 13 V at 2 000 A. At an anode current density of 10 A/sq. dm about 1 kg of fluorine is produced per hour with a current efficiency of 75 to 85 per cent. In order to remove the hydrogen fluoride from the fluorine produced the gas is cooled to — 80 °C before being led to the place of consumption. The cell containing about 600 kgs of the electrolyte after some time becomes contaminated with carbon disintegrated from the anodes, and with magnesium fluoride and magnesium silicofluoride formed by the reaction between the electrolyte and the cathode.

Harshaw's electrolyzer is another example of electrolyzer which operates at a slightly elevated temperature. (Fig. 136).

The body of the electrolyzer is made of carbon steel, covered by a jacket for heating or cooling the electrolyte. The cathode is also made of steel and perforated, to facilitate the circulation of the electrolyte. The bottom half of the diaphragm is made of Monel metal gauze soldered with silver to the upper unperforated iron part. The anodes which are arranged around the diaphragm are made of graphite rods impregnated with copper powder. The composition of the electrolyte is approximately KF . 2 HF; 1 to 1.5 per cent lithium fluoride is added in order to decrease polarization. The operating temperature of the cell is between 95 and 115 °C. Current efficiency is about 95 per cent, voltage across the cell equals 9 to 9.5 V, and the anode current density is 10 to 20 A/sq. dm. The electrolyzer is filled with some 800 kgs of electrolyte and takes 1,000—1,500 A.

Hooker tried to suppress polarization which reaches a fairly high value with carbon anodes by using a low current density. His electrolyzer was also designed to facilitate a quick replacement of worn parts in the following sequence: anodes (which suffer most quickly damage), diaphragms and cathodes.

The vessel of this electrolyzer is made of welded Monel metal fitted with a steel jacket for cooling and heating. The steel cover of the cell carries the anode and cathode assemblies and is provided with Monel metal ribs which dip some 5 cm into the electrolyte in order to separate the fluorine compartments from the hydrogen compartments. The cover is fitted with pipes for the outlet of gaseous fluorine and hydrogen as well as a pipe for the inlet of hydrogen fluoride and for purging of the vessel with nitrogen.

There are two anode assemblies in each cell. They consist of 12 carbon anode blades arranged in two parallel rows. At a current load of 4,000 A the current density at the anodes equals 13.5 A/sq. dm. The current is led to the anodes by means of copper rods which pass through stuffing boxes in the cover.

There are also two cathode assemblies suspended between the anodes. Each assembly is composed of three parallel steel plates which are suspended by means of steel rods, which at the same time serve as current conductors. These also pass through stuffing boxes in the cover of the cell.

Finally there are four wire diaphragms made of Monel metal attached to the cover. These diaphragms surround the anodes and separate them from the cathode compartment. They also prevent a short-circuit between anodes and cathodes, which might arise from small fragments of the carbon anodes.

The electrolyte, which must be extremely pure and low in moisture, contains 59 per cent potassium fluoride and 41 per cent hydrogen fluoride. When the operation commences electrolysis is allowed to proceed for some minutes at a high current density and a voltage across the cell of 30—40 V. In this way, the anodes are depolarized and then electrolysis can continue without difficulty at a voltage of 8—10 V and an anode current density of 13.5 A/sq. dm. If the anodes should become polarized during the operation, a small amount of

lithium fluoride must be added to the cell, which will suppress this undesirable effect.

A sufficient amount of hydrogen fluoride is fed into the electrolyte to maintain the initial composition of the solution corresponding approximately to the formula KF . 2 HF. Should the electrolyte contain less than 39 per cent of HF, the voltage across the cell will increase and polarization will take place. If the content of HF exceeds 43 per cent a considerable amount of hydrogen fluoride is carried away with the fluorine produced and the metallic parts of electrolyzer become quickly corroded. The compartments for collecting gaseous fluorine or hydrogen are cleansed with pure dry nitrogen in order to remove the air.

To maintain a constant temperature of the electrolyte (100—105 °C) cool water is allowed to flow through the jacket of the electrolyzer during the operation. Apart from this, there is a system of parallel tubes arranged horizontally one above the other, through which also the cooling water flows.

The cells are built for 4,000 A and operate with a current efficiency of 90 to 95 per cent. The energy efficiency is some 27 per cent. The anodes last for about 5,000 kA-hr. and the diaphragms can stand 40,000 kA-hr. while the vessel has a longer service life. The usual substances which contaminate fluorine are hydrogen fluoride (some 5 per cent), carbon dioxide, oxygen and nitrogen. The hydrogen fluoride content in fluorine can be decreased to 0.5 per cent by cooling the gas to about — 80 °C and subsequent absorption by solid sodium fluoride at 100 °C.

C. USES OF FLUORINE

Before World War II, fluorine was prepared for laboratory purposes only and was not marketed. However, during wartime a large-scale production of this gas was started in Germany. It was used for preparation of chlorine trifluoride ClF_3 with which incendiary bombs were filled. This substance is almost as chemically active as fluorine itself. Nowadays it is used as a fluorinating agent when producing some organic compounds. Fluorine is also important in the production of uranium hexafluoride, used for the separation and concentration of uranium isotopes. It is also used in the preparation of sulphur hexafluoride; this substance has a high dielectrical constant and is chemically very inactive so it can be used as a insulator in equipments working at a high voltage. Finally, fluorine is an important intermediate in the production of some polyfluorides of metals (AgF_2, CoF_3, MnF_3) which are used for preparation of fluorine derivatives of hydrocarbons.

The fluorine produced is either immediately used to prepare other final products or is first liquefied and delivered in steel cylinders where required. When fluorine is liquefied it is first led from the electrolyzer through a steel coil cooled to — 90 °C by dry ice. It then passes through a coil submerged in liquid oxygen (— 183 °C) to separate the remaining traces of hydrogen fluoride, carbon dioxide and tetrafluoromethane. The product still contains a small

amount of ozone and oxygen compounds of fluorine (OF_2, O_2F_2), which at high pressure can cause an explosion during the storage of liquid fluorine. Because of this, further purification is carried out by allowing the gas to pass through a pipe of nickel or Monel metal which is heated to 300 °C. Gas purified in this way is finally liquefied by cooling with liquid nitrogen to —191, or even —194 °C. Liquid fluorine is kept in steel cylinders of 2 or 5 litres at 150 atmospheres. The cylinders are marked by a red stripe.

XX. HYDROGEN PEROXIDE

Pure hydrogen peroxide is a colourless viscous liquid, blueish in thicker layers, with a specific gravity $s_4^\circ = 1.4649$ and a freezing point of -0.89 °C. Boiling point is very near to 151.4 °C; on boiling at a normal pressure hydrogen peroxide decomposes at first slowly, then with explosive violence. It is miscible with water in all proportions and gives a solution in which it is dissociated to a small degree into H^+ and O_2H^- ions. Pure anhydrous peroxide is only stable at 0 °C and decomposes at higher temperature. It is also very sensitive to shocks so that it cannot be transported by rail. Friction or contact with oxidizable substances also cause it to explode. During decomposition a great quantity of heat is liberated, as peroxide is a highly unstable substance from the thermodynamical point of view:

$$2\,H_2O_2(c) = 2\,H_2O(c) + O_2;\ \Delta H^\circ_{291} = -46.9\ \text{kcal}. \qquad \text{(XX-1)}$$

Even aqueous solutions of hydrogen peroxide are unstable; decomposition is accelerated by the effect of an elevated temperature and light, but mainly by the action of catalysts such as finely dispersed metals of the platinum group, silver, manganese dioxide, lead oxide, surface active agents etc. In the homogenous phase decomposition is accelerated by ions of heavy metals, hydroxyl ions but chiefly by ferments (catalases). Generally stated hydrogen peroxide in an alkaline solution is far less stable than in an acid one. The afore mentioned decomposition of hydrogen peroxide can be considerably suppressed by the addition of certain compounds known as stabilizers. Hydrogen peroxide is a strong oxidizing agent (it oxidizes for example bivalent iron, arsenites, sulphur dioxide etc.) yet it also manifests reducing properties (e. g. to silver oxide, gold trichloride, potassium permanganate etc.)

In an oxidation reaction hydrogen peroxide is reduced according to equations:

$$\text{1a)}\ H_2O_2 + 2e = 2\,OH^-;\ \pi^\circ_{OH^-,\,H_2O_2\,|\,Pt} = 0.94\ \text{V},$$

$$\text{1b)}\ H_2O_2 + 2\,H^+ + 2e = 2\,H_2O;\ \pi^\circ_{H^+,\,H_2O_2\,|\,Pt} = 1.77\ \text{V}.$$

During a reduction process the peroxide is oxidized according to equations:

$$\text{2a)}\ H_2O_2 + 2\,OH^- = 2\,H_2O + O_2 + 2e;\ \varepsilon^\circ_{Pt,\,O_2\,|\,OH^-,\,H_2O_2} = 0.15\ \text{V},$$

$$\text{2b)}\ H_2O_2 = 2\,H^+ + O_2 + 2e;\ \varepsilon^\circ_{Pt,\,O_2\,|\,H^+,\,H_2O_2} = -0.68\ \text{V}.$$

From Nernst's equation related to individual equilibrium potentials we may deduce that the oxidizing power of hydrogen peroxide, which is higher with a more positive reduction potential of the system (1b), grows with increasing concentration of the hydrogen ions in the solution. On the other hand the

reducing power of peroxide, which is higher with a more positive oxidation potential of the system (2a), increases with the concentration of hydroxyl ions.

Hydrogen peroxide reacts with some acids (sulphuric acid for instance) and forms *peroxy-acids*, and with some bases [such as $Ca(OH_2)$, $Ba(OH)_2$, $Mg(OH)_2$, $Zn(OH)_2$] and forms peroxides. Oxides of the IV and VI group of the periodic system (i. e. oxides of Ce, Ti, V, Nb, Ta, Cr, Mo, W, U) also react with hydrogen peroxide to form peroxides, peroxy-acids and persalts. Many additive compounds of hydrogen peroxide are known such as with sodium metaborate, urea and hexamethylene-tetramine.

A. THE PREPARATION OF HYDROGEN PEROXIDE FROM BARIUM PEROXIDE

Formerly, before the electrochemical process was introduced, hydrogen peroxide was produced solely by the reaction of acids with peroxides, usually barium peroxide and sulphuric acid:

$$BaO_2 + H_2SO_4 = H_2O_2 + BaSO_4 \qquad \text{(XX-2)}$$

As the economy of this process depends on possibility of marketing the barium sulphate as a pigment, this method of production is only used in a few factories today. To a greater part it was replaced by the more modern electrochemical process.

For the production according to this method, the barium peroxide must be as pure as possible and free of catalytically active impurities. It is prepared from crushed baryte, which in the first phase is reduced with bituminous coal or anthracite to barium sulphide at some 1.000 °C in a rotary kiln, heated by generator gas:

$$BaSO_4 + 4\,C = BaS + 4\,CO \qquad \text{(XX-3)}$$

The barium sulphide is leached from the calcined mass with water in a system of vats and then precipitated with soda ash to form carbonate:

$$BaS + Na_2CO_3 = Na_2S + BaCO_3 \qquad \text{(XX-4)}$$

The barium carbonate is filtered off, and the liquor is concentrated so that it yields crystalline sodium sulphide $Na_2S \cdot 9\,H_2O$ as a by-product. Barium sulphide can also be precipitated with carbon dioxide in a series of cast iron vessels. Barium carbonate, after it has been separated by filtration, is dried in a rotary dryer, heated by generator gas, and finally powdered in a rod mill.

In order to obtain light and porous barium oxide barium carbonate is mixed with petroleum coke having a low ash content or with finely ground pitch or with lamp black; this mixture is calcinated at a temperature of 1200—1300 °C in a battery of retorts heated by generator gas and placed in a brick chamber. The retorts are made of special ceramic material with addition of carborundum.

They are assembled from individual elements to form vertical tubes some 4.000 mm long with an inner diameter of about 200 mm. The escaping carbon monoxide is taken off and used for additional heating of the retorts. Calcination can also take place in crucibles, loaded on cars which automatically move through a tunnel oven. Carbonaceous materials are added to barium carbonate in order to lower the decomposition temperature of $BaCO_3$ and to increase the amount of escaping gases, which enables to obtain a porous and light product:

$$BaCO_3 + C = BaO + 2\ CO \qquad \text{(XX-5)}$$

In order to convert barium oxide into peroxide according to the reversible reaction:

$$2BaO + O_2 = 2BaO_2, \qquad \text{(XX-6)}$$

the material is heated to some 500 °C in horizontal rotary kilns into which compressed air is led. Carbon dioxide and moisture must be removed from the compressed air by passing it through a mixture of sodium hydroxide and quicklime. For the conversion, vertical cast iron tubes are sometimes used which have removable bottoms through which the reacted material can be discharged; they are externally heated by the waste heat from the tunnel oven used for the decomposition of the barium carbonate. The reaction (XX-6) is a reversible one and at an atmospheric pressure and temperature above 700 °C barium peroxide is decomposed to oxygen and barium oxide. The presence of heavy metal oxides lowers the decomposition temperature of the peroxide. It can be said, in general, that the preparation of barium peroxide with 85 to 90 per cent BaO_2 is a much simpler operation than when producing porous barium oxide.

Barium peroxide thus obtained is first ground to a fine powder and then decomposed by a 20 per cent solution of sulphuric acid to which 2—4 per cent of hydrochloric acid was added in order to increase the reaction yields.

During the process wet barium peroxide is gradually added to the sulphuric acid which is constantly stirred until the solution is almost neutral. The temperature must be maintained between 15 and 25 °C by cooling to prevent any loss of oxygen. Finally solution of barium hydroxide is added so that a slightly acid reaction to methyl orange is attained. Phosphoric acid is also admitted which causes the impurities (mainly Fe and Mn) to precipitate in the form of insoluble phosphates. The precipitated $BaSO_4$ is separated on filter presses from the clear solution which contains between 3 and 6 per cent of H_2O_2.

With a more suitable method diluted hydrochloric acid is first put into a stirred tank and then small amounts of a barium peroxide paste and of sulphuric acid are alternately added. The acid must be carefully measured, in order to maintain the solution slightly acid during the whole process and to precipitate only such an amount of sulphate which is equivalent to the amount of the barium chloride set free in the reaction between hydrochloric acid and barium peroxide. If too much sulphuric acid is added in a time, the grains of barium

peroxide become coated by the unsoluble barium sulphate formed, and so cannot be utilized for a further reaction.

The solution obtained which contains 3 to 6 per cent of H_2O_2 is too diluted for economical transport. It is, therefore, concentrated by vacuum distillation. The solution is admitted or sprayed into suitable distillation vessels at such a rate at which the vaporization can be momentarily effected. Operating temperature is between 70 and 80 °C and the operating pressure equals 60 mm Hg. The vapour is led through a condenser where a 30 per cent solution of H_2O_2 is condensed, while the water vapour enters the second condenser where it is condensed together with the small amount of remaining hydrogen peroxide.

Phosphoric acid is more advantageous than sulphuric acid for the decomposition of barium peroxide. When it is used it is possible to obtain a solution with 10 to 15 per cent of H_2O_2, because contrary to sulphuric acid even a considerably concentrated phosphoric acid ensures the satisfactory decomposition of barium peroxide. The barium phosphate $Ba_3(PO_4)_2$ formed in the process, which is easy to filter, also removes other impurities (Fe, Mn, Al etc.) if they had been converted during the final stage of the process to a less soluble form by careful neutralization of the acid solution by barium hydroxide or carbonate. The precipitate of $Ba_3(PO_4)_2$, which contains also impurities, is filtered off. The hydrogen peroxide solution obtained is fairly stable because a small amount of phosphoric acid is present.

The waste barium phosphate is dissolved in phosphoric acid to barium dihydrogen phosphate:

$$Ba_3(PO_4)_2 + 4\ H_3PO_4 = 3\ Ba\ (H_2PO_4)_2; \qquad \text{(XX-7)}$$

from this solution impurities are removed by filtration and the dihydrogen phosphate is converted to barium sulphate by a reaction with sulphuric acid:

$$3Ba(H_2PO_4)_2 + 3H_2SO_4 = 3BaSO_4 + 6H_3PO_4. \qquad \text{(XX-8).}$$

The liberated phosphoric acid is concentrated and returned to the process while the barium sulphate is sold as pigment (blanc fixe).

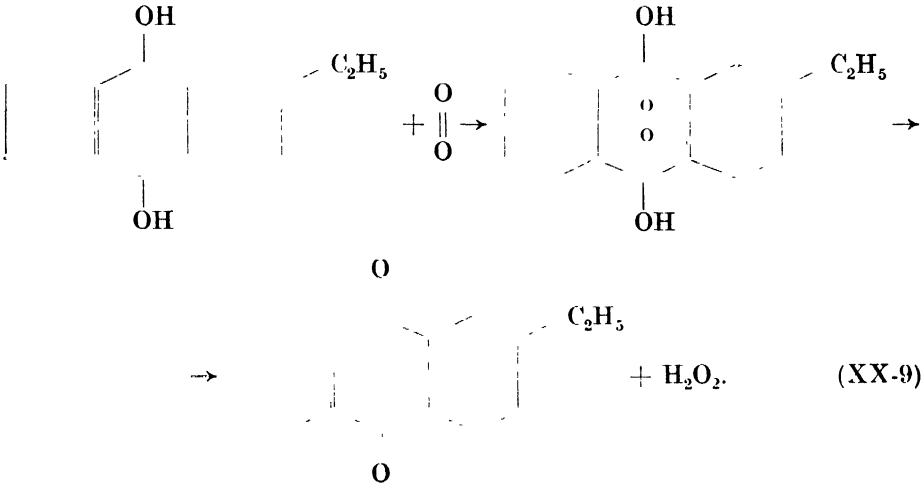
As has already been stated it is economical to produce hydrogen peroxide by this method only when there is a safe market for the by-product (blanc fixe). As there was an increased demand for hydrogen peroxide but not for barium sulphate, it is not surprising that the above method had to give way to other modern methods.

B. THE MANUFACTURE OF HYDROGEN PEROXYDE FROM ETHYLANTHRAQUINONE

A very interesting new method was developed by I. G. Farben in Germany during the World War II. In this method 2-ethylanthrahydroquinone is oxidized by gaseous oxygen whereby 2-ethylanthraquinone and hydrogen peroxide are formed. Hydrogen peroxide is extracted from the resultant liquor with water

and anthrahydroquinone is regenerated by catalytic hydrogenation of the anthraquinone.

The first production stage is effected in a series of closed enamelled iron kettles filled with a mixture of equivalent amounts of 2-ethylanthraquinone and 2-ethylanthrahydroquinone dissolved in benzene and methylcyclohexanol; oxygen is injected into the liquid through a porous filter while the temperature is maintained at 30 and 37 °C. The reaction may be symbolized as follows:



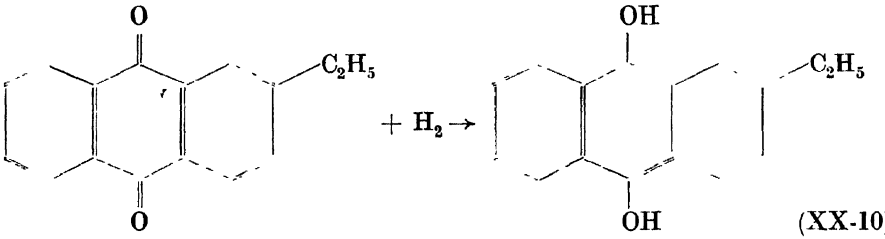
(XX-9)

Hydrogen peroxide is extracted with water from the reaction liquor; the final product so obtained contains some 20 per cent of hydrogen peroxide. Extraction is carried out in a tower in which the water flows in a downward direction over trays while the solution of quinone passes countercurrently upwards. The small amount of water remaining in the quinone phase is removed in another tower by extraction with a concentrated solution of potassium carbonate (33 to 50 per cent); finally all traces of hydrogen peroxide are eliminated by allowing the liquor to pass over a porous material on the surface of which metallic nickel and silver were deposited; following this the liquor is filtered and regenerated.

The regeneration of 2-ethylantraquinone is effected by hydrogenation at a normal temperature and at a slightly elevated pressure (1-2 atmospheres). This operation takes place in closed aluminium reactors, 1800 mm in diameter and 2100 mm high, in presence of Raney nickel*) as a catalyst. Reactors

*) Raney's nickel is prepared by dissolving an alloy of nickel and aluminium in a solution of sodium hydroxide; the aluminium dissolves while the nickel remains in a metallic state as a highly dispersed phase; the dispersed metal is separated by filtration and used as a catalyst.

are fitted with a stirrer and have porous ceramic candle filters arranged at the sides through which the product is filtered after reaction. Hydrogen used for regeneration must not contain carbon monoxide or sulphur compounds. The reaction proceeds in accordance with the following equation:



(XX-10)

Reaction is stopped as soon as the original quinone is reduced by half so that the reaction product is a mixture of anthraquinone and anthrahydroquinone, which is returned to the first stage of production for oxidation.

This process was developed in Germany during the war to avoid the use of platinum which is necessary for the electrochemical method. According to available reports the operation was very dangerous and an accident which occurred during research cost the life of all personnel working in the vicinity of the pilot plant. The final product contained small admixtures of organic compounds and could not be concentrated to 80 per cent H_2O_2 owing to the danger of explosion. The entire oxidation and reduction process took about two hours. The yields related to the hydrogen consumed amounted to 90 p. c.

According to more recent research hydrazobenzene and hydrazotoluene can also be used as hydrogen donors to oxygen. The azobenzene or azotoluene resulting from oxidation are reduced to the initial hydrazo-compounds by sodium amalgam.

C. THE MANUFACTURE OF HYDROGEN PEROXIDE BY SILENT ELECTRIC DISCHARGE

This method which has already been known for some time, was restudied during the war by the firm of *Elektrochemische Werke* in Munich, Germany. According to reports it has been tested at a pilot plant rated of 2000 kw. The process is based upon the fact that through the influence of silent electric discharge on a nonexplosive mixture of hydrogen with a maximum of 5 per cent oxygen, hydrogen peroxide is formed by the combination of the hydrogen atoms, from the split molecules, with molecular oxygen. To increase the yield a small quantity of water vapour is admitted to the gaseous mixture. It is a cyclic process; after the reaction mixture has passed through the ionisation chamber the hydrogen peroxide is separated as a 10 p. c. solution; the remaining gases are mixed with fresh hydrogen and oxygen electrolytically produced and recirculated.

As can be seen from the schematic representation in Fig. 137 a gaseous mixture of hydrogen and some 5 per cent oxygen saturated with steam at 60 °C is blown by means of fan *A* at a pressure slightly over one atmosphere through heat exchanger *C* into the ionisation chamber *B*. In the chamber there are a great number of parallel quartz plates which are coated with a layer of aluminium on the outside, and etched with hydrofluoric acid on the inside. The plates (500 × 500 mm, 5 mm thick) are arranged with the etched sides opposite to each other at a distance of 5 mm apart. The aluminium coated sides of the plates are connected in parallel to the source of alternating current with 9 500 cycles and a voltage of 12000 V. At 2000 kw and a specific input of 0.96 kw per pair of plates 4420 plates are required at all. The average temperature in the ionisation chamber is 160 °C.

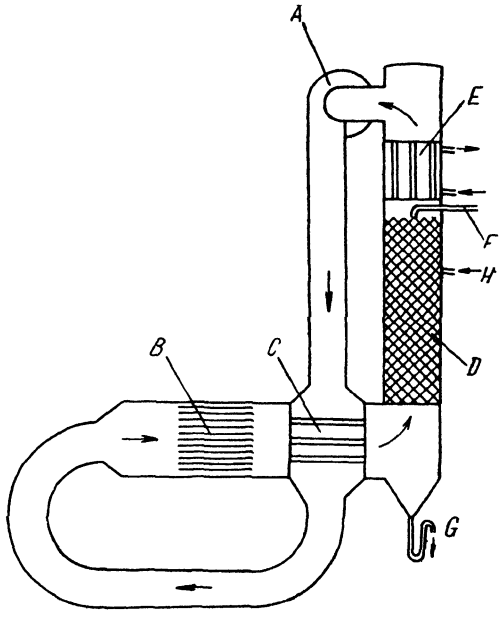


Fig. 137. Schematic diagram of the production of hydrogen peroxide by silent electric discharge.

A — Ventilator, *B* — Ionisation chamber, *C* — Heat exchanger, *D* — Rectifying column, *E* — Condenser, *F* — Distilled water inlet, *G* — Trap for draining H_2O_2 solution, *H* — Admission of oxygen and hydrogen from gas-holder.

The reacted gases first stream through heat exchanger *C* and heat the new mixture entering the ionisation chamber. Then they are led into rectifying column *D* filled with Raschig rings on the top of which is mounted a tubular water condenser *E*. At point *F* distilled water is admitted to the column, which absorbs the hydrogen peroxide and leaves through the trap *G* in the form of a 10 per cent solution. Make up hydrogen and oxygen are introduced at point *H*. The cooled gases are sucked by ventilator *A* and recirculated. The 10 per cent solution obtained can be readily distilled to give a final product containing 30—35 per cent H_2O_2.

The above described apparatus with a power input of 2.000 kw produces about 50 kgs of hydrogen peroxide per hour (calculated as a 100 per cent product). The total energy consumption — including energy necessary for the electrolytical production of hydrogen and oxygen, to drive the ventilator and auxiliary equipments — makes 62.6 kw-hr per 1 kg of 100 per cent H_2O_2. Compared with this, the total energy consumption necessary for the electro-

chemical production of hydrogen peroxide is about 18 kw-hr per 1 kg of 100 per cent H_2O_2, which is less than one third of the former. The method described, however, yields an extremely pure product, and moreover, the operational control is simple. It is probable that in the future it may be possible to lower the high energy consumption in which case the process would be competitive to the electrochemical process.

D. MANUFACTURE OF HYDROGEN PEROXIDE BY THE ELECTROCHEMICAL PROCESS

Hydrogen peroxide is produced on a large scale mainly by distilling persulphuric acid or persulphates with sulphuric acid.

1. Theoretical principles of the preparation of persulphuric acid and persulphates:

Persulphuric acid or persulphates are produced by the oxidation of sulphuric acid or sulphates at an anode of smooth pure platinum using a high current density. Only smooth platinum can be used for the anodes because no other material displays such a high oxygen overvoltage.

a) *Electrolysis of sulphuric acid*

The standard equilibrium potential of the oxygen electrode, corresponding to the reaction

$$2\ OH^- = \tfrac{1}{2}\ O_2 + H_2O + 2e, \qquad \text{(XX-11)}$$

is

$$\pi^\circ_{OH^-\,|\,O_2,\,Pt} = 0.401\ V.$$

Owing to the overvoltage oxygen is deposited on all metals at potentials which are higher than the equilibrium potential. When smooth platinum is used, which displays an overvoltage ranging from 0.8 to 1.4 V, according to the current density, the oxygen is deposited only at potentials between 1.2 to 1.8 V (from a solution with $a_{OH^-} = 1$).

The following electrode reaction

$$2\ OH^- = H_2O_2 + 2e, \qquad \text{(XX-12)}$$

in the course of which hydrogen peroxide is formed by the discharge of two hydroxyl ions, shows a potential $\pi^\circ_{OH^-,\,H_2O_2\,|\,Pt} = 0.94$ V. As this potential is lower than the deposition potential of oxygen it might be assumed at first sight that when using anodically polarized smooth platinum, hydrogen peroxide could be directly obtained by the electrolysis of diluted hydroxide or even water. Actually, this oxidation cannot take place, because the peroxide formed would be immediately decomposed at the anode according to equation:

$$H_2O_2 + 2\ OH^- = O_2 + 2\ H_2O + 2e \qquad \text{(XX-13)}$$

as this process occurs at a potential $\pi^{\circ}_{OH^-,\,H_2O_2\,|\,Pt,\,O_2} = -0.15$ V which is much lower than that of reaction (XX-12).

The liberation of oxygen can, however, be supressed considerably if sulphuric acid is used as the electrolyte, which is anodically oxidized into persulphuric acid. From what has been said about the formation of persulphate ions (see theoretical section) it is clear that the anodic process can be expressed by the following overall equation:

$$2SO_4^{--} = S_2O_8^{--} + 2e. \qquad \text{(XX-14)}$$

Pure persulphuric acid unlike hydrogen peroxide is entirely stable against further oxidation at the anode. However, the sulphuric acid undergoes the hydrolysis and so decomposes to a small extent to Caro's acid and hydrogen peroxide, i. e. compounds which liberate easily their oxygen fixed by the peroxide linkage. Hydrolysis which proceeds according to e quations:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4 \qquad \text{(XX-15)}$$

$$H_2SO_5 + H_2O = H_2SO_4 + H_2O_2 \qquad \text{(XX-16)}$$

is promoted by the presence of free sulphuric acid and by an elevated temperature. The higher the concentration of sulphuric acid the higher the rate of hydrolysis of the persulphuric acid; at the same time sulphuric acid increases the rate of reaction (XX-15) much more than that of (XX-16). As both reactions are reversible, a certain equilibrium will be established between the individual reaction components, which depends upon the given reaction conditions.

It has already been stated that the products of hydrolysis of persulphuric acid are not stable but react with one another under the liberation of oxygen:

$$H_2SO_5 + H_2O_2 = H_2SO_4 + O_2 + H_2O. \qquad \text{(XX-17)}$$

Apart from this, Caro's acid is also decomposed electrochemically at the anode under the liberation of oxygen:

$$H_2SO_5 + 2OH^- = H_2SO_4 + O_2 + H_2O + 2e. \qquad \text{(XX-18)}$$

This process causes depolarization of the anode as it proceeds more easily than reaction (XX-14). Caro's acid is, therefore, harmful not only for causing a loss in active oxygen but also for its depolarizing effect, which lowers the necessary high anode potential whereby current efficiency is decreased. For this reason electrolysis should be carried out under conditions which suppress as much as possible the hydrolysis of persulphuric acid according to equations (XX-15) and (XX-16) and, therefore, the secondary reactions (XX-17) and (XX-18).

Apart from oxygen which is liberated by the decomposition of Caro's acid according to equation (XX-18) a certain amount of oxygen is also formed by

the direct discharge of hydroxyl ions according to equation (XX-11). If the process is carried out in rather acid solution, with a very low concentration of hydroxyl ions, current losses due to the last reaction are small. The oxygen formed always contains a small amount of ozone.

Other current losses may be caused by the reduction of persulphate ions at the cathode. In order to prevent this the anode and cathode must be separated by a diaphragm.

At a cathode which dips into an acid solution the hydrogen ions are reduced to gaseous hydrogen:

$$2H^+ + 2e = H_2 \qquad \text{(XX-19)}$$

On combining equations (XX-19) and (XX-14) we obtain an equation expressing the whole process of electrolysis of sulphuric acid:

$$2H^+ + 2SO_4^{--} = S_2O_8^{--} + H_2 \qquad \text{(XX-20)}$$

or:

$$2H_2SO_4 = H_2S_2O_8 + H_2. \qquad \text{(XX-20a)}$$

If we disregard the by-products, the products of electrolysis according to the last equation are persulphuric acid and hydrogen.

α) Effect of sulphuric acid concentration and anode current density

Current efficiency first increases with an increased concentration of sulphuric acid; at a specific gravity from 1.3 to 1.5 it attains top value but decreases afterwards. This dependence clearly indicates that two competitive processes are involved. Efficiency increases first because of a greater concentration of sulphate ions, in latter stages the decomposing effect of sulphuric acid upon persulphuric acid prevails. Very important is the current density which, increasing itself, causes an increase of the anode potential and of the current efficiency. This favourable effect is limited, as, after a certain optimum value is reached, current efficiency begins to decrease, probably due to an increased temperature of the anode resulting from too high current density. The optimum value of current density depends upon the concentration of sulphuric acid. The higher the concentration, the lower the optimum current density, and vice versa.

At the beginning of the electrolysis of sulphuric acid, oxidation occurs mainly according to equation (XX-14) with a relatively high current efficiency (65 to 76 per cent depending upon concentration and current density). With an increased concentration of persulphuric acid in the solution, the rate of hydrolysis to Caro's acid according to (XX-15) also increases. Caro's acid is then decomposed according to equation (XX-18), whereby the anode potential is lowered and consequently less persulphuric acid is formed. In later stages of

electrolysis the situation becomes so unfavourable that the current efficiency calculated for active oxygen not only drops to zero, but becomes actually negative (i. e. the amount of persulphuric acid in the electrolyte decreases). This takes place when the amount of fresh persulphuric acid formed at the anode proves insufficient to replace its losses due to decomposition which proceeds through Caro's acid. Evidently the solution contains the greatest amount of persulphuric acid at the moment when the current efficiency equals zero. This maximum depends upon operating conditions and the concentration of the acid. (In a series of tests performed at 15 °C, a maximum concentration of persulphuric acid was obtained at anode current density of 200 A per sq. dm. and at a current concentration of 30 A/litre when sulphuric acid with specific gravity 1.3 was used). The same factors also govern the current efficiency during the initial stages of electrolysis (under the above mentioned conditions the best efficiency was 76 per cent, provided sulphuric acid with a specific gravity 1.42 was used.). The average current efficiency from the beginning of the electrolysis until the moment when it reaches zero is comparatively low, its maximum being about 40 per cent. The efficiency can be substantially raised by the addition of certain substances to the electrolyte (see later).

β) The effect of temperature

The lower the temperature of the electrolyte, the lower the rate of hydrolysis (XX-15) and (XX-16), which causes a loss in active oxygen according to reactions (XX-17) and (XX-18). Apart from this, a low temperature increases the oxygen overvoltage and, therefore, also the anode potential to the necessary high value. In order to maintain a low temperature (between 20 and 30 °C) the electrolyte must be cooled very efficiently as the liberation of heat is considerable owing to the high current densities used. Because good cooling mainly in the boundary layer between the anode and the bulk of the electrolyte is very important some cells have hollow anodes which are cooled internally by water. In some instances the cathodes also are cooled in the same manner. To maintain low temperature when producing persulphuric acid is much more important than when producing ammonium persulphate.

γ) The effect of additives

A still more favourable effect upon current efficiency is achieved if certain substances such as fluorides are added, which raise the potential by some hundredths or even tenths of a volt. Other compounds such as chlorides, cyanides (potassium cyanide, ferrocyanide or ferricyanide) or thiocyanates have a double effect: on one hand they decompose the Caro's acid and on the other hand they raise the anode potential. Ammonium thiocyanate is almost generally used. It reduces Caro's acid, at first, and changes it into sulphuric acid and hydrogen cyanide, the latter promoting a rise in the anode potential.

δ) The effect of current concentration

Current efficiency can also be improved by removing the product of the electrolysis, i. e. the persulphuric acid from the electrolyzer, before decomposition to Caro's acid can take place to any great extent. In order to attain a sufficient concentration of persulphuric acid in the electrolyte, the anodic compartment is made narrower whereby current concentration may be increased at unchanged current density. Thus, the higher the current concentration used, the shorter the time required to increase the concentration of persulphuric acid to the desired value, and the shorter the time during which the acid is subject to undesirable hydrolysis. In practice, electrolysis is carried out in a continuous manner, the electrolyte being allowed to flow at great speed through the narrow anode space at a current concentration of 300 to 500 A per litre.

ε) Influence of the cations

We have been discussing electrolysis of pure sulphuric acid. We have found that the more of the sulphuric acid will be replaced by sulphates, the higher current efficiency will be attained. Ammonium sulphate is the most effective salt as it gives relatively the most soluble persulphate and secures an optimum current efficiency, which may reach 95 per cent when solutions of ammonium sulphate alone are used.

The reason for improved current efficiency lies in the fact that mixed solutions of sulphuric acid and sulphates have a lower concentration of free sulphuric acid, so hydrolysis of persulphuric acid and persulphates proceeds at a much slower rate which results in considerably less Caro's acid being formed.

b) *Electrolysis of a neutral solution of ammonium sulphate*

From what has been said about the influence of the cations it follows that the highest current efficiency is obtained when electrolysis is carried out with a neutral solution of ammonium sulphate. With such a solution the formation of harmful Caro's acid is almost entirely avoided. Another advantage of a neutral solution is that no diaphragm is needed to prevent the reduction of persulphate at the cathode. The addition of a small amount of alkali chromate to the solution will suppress reduction as a thin film of chromium hydroxide is formed on the cathode surface which prevents the persulphate ions coming into contact with the electrode.

The overall process of electrolysis of ammonium sulphate can be expressed by the following equations:

cathode: $2\,NH_4^+ + 2\,H_2O + 2e = 2\,NH_4OH \uparrow H_2$, (XX-21)

anode: $2\,SO_4^{--} = S_2O_8^{--} + 2e$, (XX-22)

total: $2\,NH_4^+ + 2\,SO_4^{--} + 2H_2O = S_2O_8^{--} + 2\,NH_4\,OH + H_2$

or (XX-23)

$2(NH_4)_2SO_4 + 2\,H_2O = (NH_4)_2S_2O_8 + 2\,NH_4OH + H_2$ (XX-23a)

It can be clearly seen from the last equation that in the course of electrolysis the catholyte becomes alkaline and the ammonia which has been set free can escape into the ambient atmosphere. Further losses of ammonia are caused by its anodic oxidation to nitrogen or nitrate. Another difficulty is caused by the hydroxyl ions, which in an alkaline solution also take part in the conduction of current and are then discharged at the anode, which reduces the current efficiency.

To prevent the undesirable processes mentioned above, it would be necessary to maintain during electrolysis a neutral reaction by gradually introducing just the right amount of concentrated sulphuric acid into the stirred electrolyte to neutralize the ammonia. As, however, this measure is industrially difficult to comply with, the method of operating in a neutral solution is not suitable for commercial exploitation.

c) *Electrolysis of acid ammonium sulphate solutions*

Contrary to the method which starts with a neutral solution of ammonium sulphate, electrolysis of an ammonium sulphate solution acidified by sulphuric acid does not present any technical difficulty, as an electrolyte containing a sufficient amount of the free acid will never become alkaline. However, it should be noted that the advantage which consists in easy working and operational control is offset by a certain diminishing of the current efficiency as with free sulphuric acid present in the electrolyte the undesirable hydrolysis of persulphuric acid to Caro's acid will occur to a certain extent.

Reactions taking place at the cathode and at the anode can be expressed by the following equations:

cathode:	$2H^+ + 2e = H_2$	
anode:	$2SO_4^{--} = S_2O_8^{--} + 2e$	
total:	$2H^+ + 2SO_4^{--} = S_2O_8^{--} + H_2,$	
or:	$(NH_4)_2SO_4 + H_2SO_4 = (NH_4)_2S_2O_8 + H_2.$	(XX-24)

From electrolysis solutions can be obtained with a maximum concentration of 250 g per l. $(NH_4)_2\,S_2O_8$. Higher concentrations are not advisable, as the persulphate would crystallize out in the electrolyzer.

As in a strongly acid medium the chromite film would dissolve, it is necessary to separate the anolyte from the catholyte. Either an acid resisting diaphragm (according to Loewenstein) is used for this purpose, or in less concentrated persulphate solutions the cathode is enveloped in asbestos (according to Adolph Pietsch). Diaphragms, however, cause an increased cell voltage.

2. Theoretical principles of the distillation of persulphates and of the fractional condensation of $H_2O_2 - H_2O$ vapours

Hydrogen peroxide is obtained from persulphuric acid or persulphate solutions by vacuum distillation. However, before hydrogen peroxide can be distilled,

it must be set free by hydrolysis of the peroxy-compounds present. The rate of hydrolysis will be increased with an elevated temperature, and by the presence of free sulphuric acid. Hydrolysis proceeds in the following two stages:

$$H_2S_2O_8 + H_2O = H_2SO_5 + H_2SO_4, \quad \text{(XX-25)}$$

$$H_2SO_5 + H_2O = H_2O_2 + H_2SO_4. \quad \text{(XX-26)}$$

It can be seen from these two equations that the processes are identical with those occurring during electrolysis. However, whilst in electrolysis these reactions were regarded as detrimental they are necessary for the separation of H_2O_2 from a solution of persulphuric acid or persulphates.

The hydrolysis of persulphates or persulphuric acid to Caro's acid is the first process and only afterwards further decomposition to hydrogen peroxide takes place. The second reaction is incomplete and the degree of hydrolysis of Caro's acid to hydrogen peroxide depends on the concentration of water in the system. When distillation is performed in externally heated stills, mainly water is first evaporated, so that the concentration of persulphuric acid and of products of its hydrolysis in the distillation residue increases at first. The amount of hydrogen peroxide in vapours rises slowly with the continuation of the process until about half of the liquor is vaporized; then its distillation proceeds rapidly. The distillation is usually continued till some six or seven tenths of the original volume of the electrolyte are distilled off. The distillation residue is a concentrated solution of sulphuric acid or of ammonium hydrogen sulphates in which further hydrolysis of the remaining persulphuric and Caro's acid ceases owing to a lack of water. Distillation is, therefore, discontinued. The distillation residue is diluted with water and distilled again, or else, direct steam is introduced into it in a special distillation retort. After redistillation the active oxygen content is sufficiently low in the final distillation residue.

At room temperature persulphuric acid decomposes to hydrogen peroxide at a very low rate. Although a rise in temperature accelerates the decomposition yet a simultaneous loss of active oxygen is brought about by the following secondary reactions:

$$H_2S_2O_8 + H_2O_2 = 2\,H_2SO_4 + O_2, \quad \text{(XX-27)}$$

$$H_2SO_5 + H_2O_2 = H_2SO_4 + H_2O + O_2. \quad \text{(XX-28)}$$

Because of these reactions the distillation of persulphuric acid and persulphate solutions present a difficult technical problem. First of all, the solutions used for the distillation must be as free as possible of catalytically active substances (such as salts of iron, manganese, copper etc.) as they would considerably promote the decomposition of peroxide. Secondly, satisfactory results require a sufficiently high rate of distillation. A quick heating of the solution to boiling point and a quick removal of the vapours formed from the distillation space means that the time during which the peroxide is in contact with the persulphuric and Caro's acid and the time of the catalyst action are considerably

shortened. Thus undesirable reactions (XX-27) and (XX-28) will be suppressed to a limited extent. Distillation must proceed under reduced pressure at temperatures ranging from 60 to 80 °C as a temperature around 90 °C causes decomposition of the hydrogen peroxide.

Apart from peroxide a considerable amount of water is also vaporized during distillation. This is why the concentration of hydrogen peroxide in the vapour is relatively low, so that simple condensation would only yield a comparatively diluted solution (the process of the Österreichische Chemische Werke would yield a 7 per cent solution and the Loewenstein process a 3 per cent solution). The possibility of obtaining a concentrated solution by using a fractional condensation of vapour is based on much lower vapour pressures and higher boiling points of hydrogen peroxide and its aqueous solutions, compared with pure water. Consequently, any vapour mixture H_2O_2—H_2O has a lower concentration of hydrogen peroxide at any condensation temperature and at any pressure than the liquid phase, both phases being in equilibrium. Thus, e. g. when at a pressure of 30 mm Hg and at 36.9 °C, a vapour mixture containing 2 per cent b. w. H_2O_2 begins to condense the first portion of the condensate contains 32.5 per cent b. w. H_2O_2. Condensation of a vapour mixture with 3 per cent b. w. of H_2O_2 will set in at the same pressure as in the previous instance at a temperature of 38.4 °C, at which the condensate in equilibrium with the vapour phase contains 39 per cent b. w. H_2O_2. Vapours containing 5 per cent b. w. H_2O_2 begin to condense at 40 °C, and the first portions of the condensate will contain 46 per cent b. w. of H_2O_2.

In order to condense further portions of vapour, it is necessary to lower the temperature, which will always cause an increasing amount of water to pass into the condensate and so lower the peroxide concentration. If a maximum of the hydrogen peroxide is to be obtained by fractional condensation as a solution, concentrated as much as possible, the condensation must be performed methodically in rectifying columns with bubble trays or in columns packed with Raschig rings, where the vapours H_2O_2—H_2O come in contact with countercurrently flowing pure water or the condensate of vapour leaving the fractionating columns. This condensate will be a very diluted aqueous solution of hydrogen peroxide. Through the cooling effect of the descending reflux the required temperature drop in the columns is maintained. Through the rectification effect of the reflux the ascending vapour mixture H_3O_2—H_2O, on approaching the top of the column is enriched with the more volatile component, i. e. with water vapour, whilst the content of the less volatile component, i. e. hydrogen peroxide is reduced. On the other hand the peroxide vapour on passing through the column is gradually condensed and leaves the bottom of the column as a concentrated aqueous solution of hydrogen peroxide. At the outlet of the column, where the temperature is relatively the highest, the concentration of the solution corresponds approximately to the equilibrium between the liquid phase and the vapour mixture at a temperature at which the initial vapour mixture begins to condense. Thus e. g. from a mixture containing 3 per cent

b. w. H_2O_2 which at a pressure of 30 mm Hg would theoretically yield a condensate with 38.4 per cent b. w. H_2O_2, in practice a condensate containing 35 per cent b. w. H_2O_2 will be obtained. The uncondensed vapour which escapes from the top of the column and contains only traces of hydrogen peroxide is condensed in a cooler; this condensate is frequently used as reflux for the rectifyng columns.

On combining equation (XX-20a) or (XX-24) and (XX-25) with equation (XX-26) the following overall equation will be obtained which expresses the overall electrolytic and distillation processes:

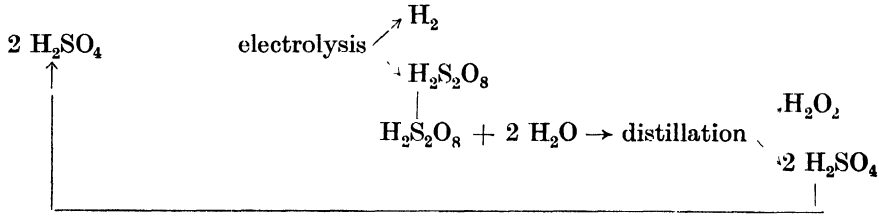
$$2\ H_2O = H_2O_2 + H_2. \qquad \text{(XX-29)}.$$

From this equation it is obvious that water is the only raw material in the manufacture of hydrogen peroxide. The other chemicals H_2SO_4, $(NH_4)_2\,SO_4$ etc. are auxiliary substances which return to the production cycle and are added only in an amount necessary to replace mechanical losses.

3. Methods of manufacturing hydrogen peroxide

a) *Process of the Österreichische Chemische Werke, Weissenstein*

By this method a solution of sulphuric acid is oxidized to persulphuric acid which is then distilled under reduced pressure to yield hydrogen peroxide. The cyclic process is represented by Fig. 138 and the following diagram:



The electrolyzer system has 26 to 27 units which are arranged in cascades. The initial electrolyte containing about 500 g H_2SO_4 per litre first passes through the cathode chambers of the electrolyzers. It is then pumped to the top of the cascade, passes through anode chambers and leaves as a solution containing 250 g $H_2S_2O_8$ per litre. The purpose of this combined flow is to remove, by reduction at the cathode, all Caro's acid remaining in the electrolyte after distillation, which would reduce the anode current efficiency related to the production of persulphate. Moreover, by the use of such an arrangement any permanent change in the electrolyte composition, caused by the migration of the ions through the diaphragm will be avoided. In the course of electrolysis the hydrogen ions migrate from the anode to the cathode, while HSO_4^- and SO_4^{--} ions migrate in the opposite direction. With the migration of sulphate ions and the discharge of hydrogen ions at the cathode the concentration of

sulphuric acid diminishes in the catholyte. In the anode compartment the number of hydrogen ions would rapidly decrease, if persulphates were exclusively formed at the anode. Since, actually a certain amount of oxygen is also evolved at the electrode and an equivalent amount of sulphuric acid formed simultaneously, the decrease in hydrogen ions in the anolyte caused by migration towards the cathode is only displayed to a limited extent.

If the electrolyte would be introduced for oxidation directly into the anode compartment, the concentration of sulphate ions would be higher after each passage through the electrolyzer. This method would, however, make it imposible to operate continually. To avoid this, the electrolyte is first allowed to pass through the cathode chambers of the electrolyzer where it loses a certain amount of sulphate ions by transference. The solution is then again pumped to the top of the cascade in order to pass through the anode chambers. Here, the sulphate ions which the electrolyte has lost while acting as a catholyte will be regained. Thus, the amount of sulphate ions including persulphate ions formed by oxidation is maintained at a constant level.

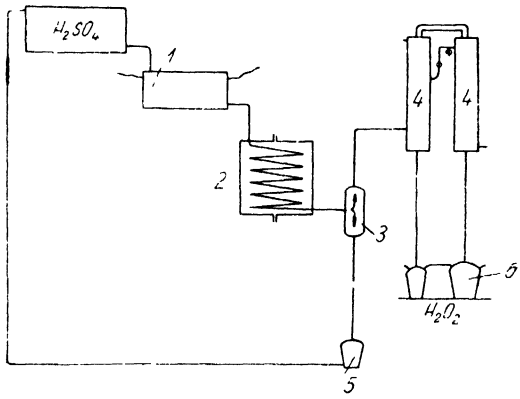


Fig. 138. Weissenstein process (flow sheet).
1 — Electrolyzer, *2* — Evaporator — *3* — Separator of acid from vapour, *4* — Condensers, *5* — Receiver for separated acid, to be recycled to the electrolyzer, *6* — Piping to the vacuum pump.

Electrolyzer *1* (see Fig. 139) is a stoneware vessel (a tank for 1000 A having internal dimensions 980 × 150 × 500 mm) with overflows for the anolyte *4* and the catholyte *2*.

As a rule, the tank contains 10 cylindrical diaphragms *3* (each 500 mm long and 50 mm in internal diameter). On the outside, lead coils *14* are wound round the diaphragms. Water passes through the coils which simultaneously act as cathodes. Glass cylinder *5* is inserted into the inner space of each diaphragm. Through the closed bottom of the cylinder a glass tube *6* passes, communicating at point *7* with the narrow, annular anode space *8*.

In the anode space platinum foils *12* are suspended, pressed on tantalum strips and fastened to lead ring *9* which holds the glass cylinder *11*. Through a polyvinyl chloride hose *17* and elbow *16* cooling water is introduced into coil *14*, leaves it through elbow *19* and enters glass tube *20* which nearly reaches the bottom of glass cylinder *5*. Ultimately the cooling water leaves through overflow *13*. In this manner, both catholyte and anolyte are cooled in the annular space *8*.

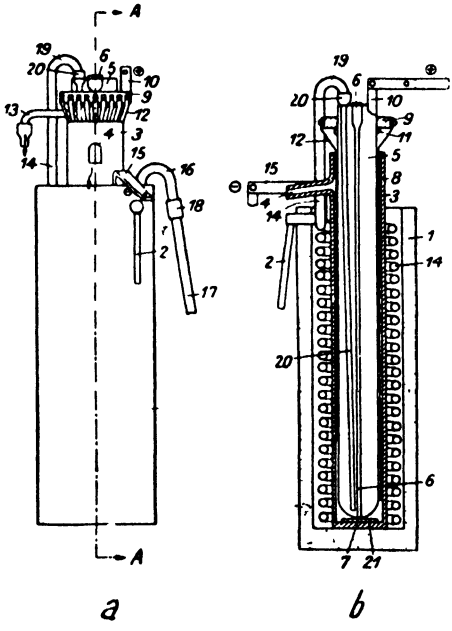
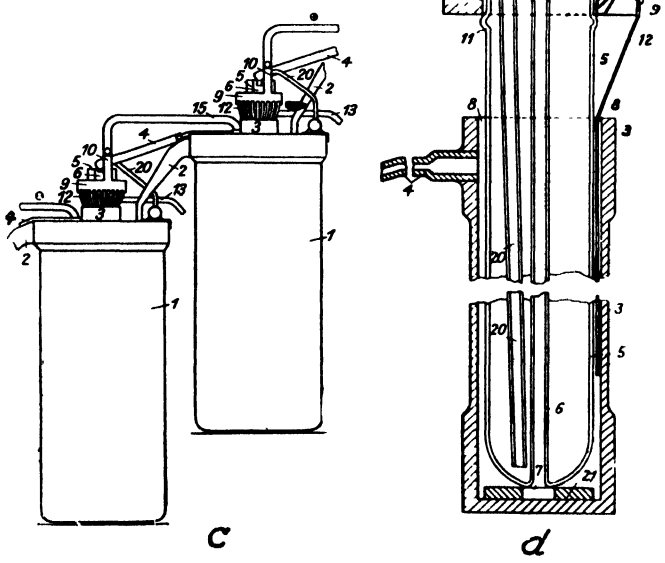


Fig. 139. Weissenstein cell for the manufacture of hydrogen peroxide.

a — Elevation, *b* — Section A—A, *c* — Connection of cells, *d* — Position of anode in the anode compartment of the cell, *1* — Stoneware tank of the cell, *2* — Catholyte overflow, *3* — Cylindrical diaphragm, *4* — Anolyte overflow, *5* — Glass cylinder, *6* — Glass pipe for inlet of electrolyte, *7* — Communicating opening, *8* — Anode chamber, *9* — Lead ring to fasten anode foils, *10* — Positive pole connection, *11* — Shoulder of the glass cylinder to support lead ring, *12* — Anode foil, *13* — Cooling water overflow, *14* — Lead cooling coil acting as the cathode, *15* — Negative pole connection, *16* — Polyvinyl chloride elbow, *17* — Polyvinyl chloride tube, *16, 17* — Hose introducing cooling water into lead coil, *14, 18* — polyvinyl chloride connection, *19* — Cooling water outlet from lead coil, *20* — Glass tube for inlet of cooling water to glass cylinder, *21* — Disk supporting the glass cylinder.



The anolyte is introduced into the electrolyzer through a narrow tube *6* and after being preliminary cooled it enters the anode space at point *7*, and leaves the space through overflow *4*. The catholyte flows into the electrolyzer situated below, through overflow *2*.

The cell operates with a high current concentration which may reach 300 to 500 A per litre. The anolyte flows at a high velocity along the platinum anodes

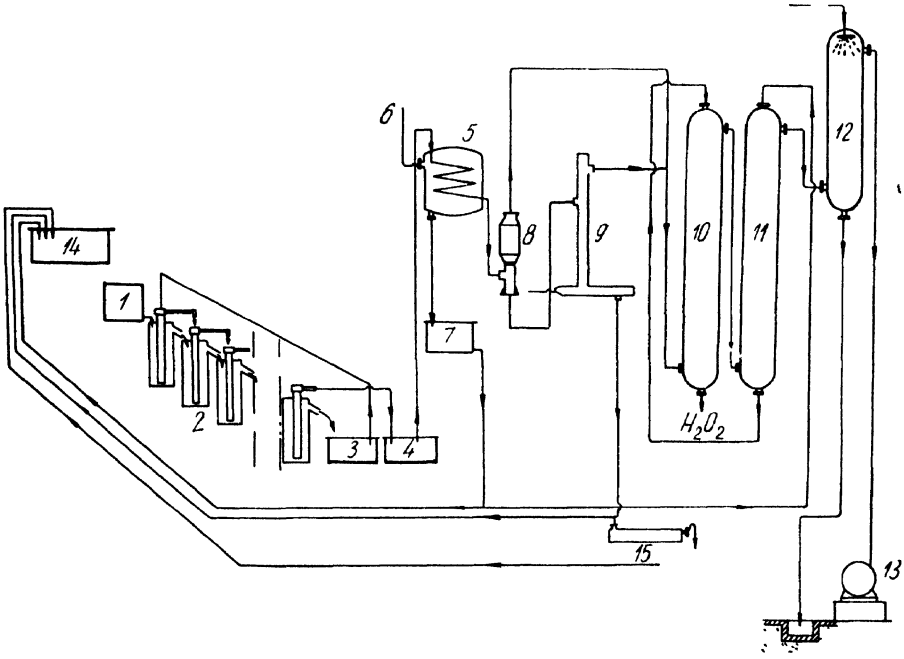


Fig. 140. Flow sheet of manufacture of hydrogen peroxide from persulphuric acid. *1* — Electrolyte container, *2* — Cells, *3* — Catholyte container, *4* — Anolyte (persulphuric acid) container, *5* — Lead distillation coil, *6* — Heating steam inlet, *7* — Tank for steam condensate, *8* — Separator of liquid from vapour, *9* — Auxiliary distillation equipment, *10* — Main column for fractional condensation, *11* — Second column, *12* — Barometric condenser, *13* — Vacuum pump, *14* — Acid dilution vessel, *15* — Acid purifier.

while on the other side of the diaphragm the catholyte moves at a relatively low velocity around the cooled lead coil. In this way a low temperature is maintained in the cell and the undesirable accumulation of heat is avoided. The current density at the anodes amounts to 60 to 80 A per sq. dm and at the cathodes 10 A per sq. dm. Each electrolyzer takes 100 A so that the whole system which contains 10 elements is loaded with 1,000 A. Voltage across the terminals of one cell amounts to 5.0 to 5.5 V. Modern electrolyzers are built for 5,000 to 10,000 A.

The temperature of the anolyte is between 20 to 30 °C. In order to increase current efficiency, a small amount of ammonium thiocyanate is added to the electrolyte. Owing to a high current concentration, effective cooling of the electrolyte and the admixture of ammonium thiocyanate current efficiency reaches 70 to 75 per cent.

The solution obtained which contains some 250 g $H_2S_2O_8$ and 280 g free H_2SO_4 per litre is led through a distillation lead coil externally heated with steam. The mixture of water and hydrogen peroxide vapours with the entrained liquid (some 60 per cent of the original electrolyte volume has been vaporized) is first introduced into a separator, where the liquid phase is separated from the vapour mixture. The remaining hydrogen peroxide is removed from the separated liquid by stripping with direct steam in an auxiliary distillation column. The bottom liquid, i. e. the sulphuric acid, concentrated to some 75 per cent after distillation, is almost free of active oxygen. It is then diluted and is recycled into the electrolytic process while a certain portion is purified by distillation carried out in a quartz equipment.

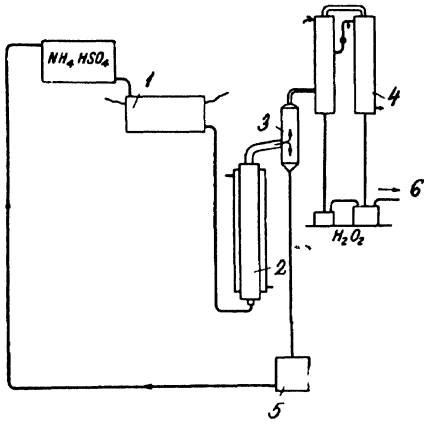


Fig. 141. Flow sheet of Loewenstein process.

1 — Electrolyzer, *2* — Evaporator, *3* — Separator of liquid from vapour, *4* — Hydrogen peroxide condensers, *5* — Separated solution of ammonium hydrogen sulphate which is recycled to the electrolysis, *6* — Piping to vacuum pump.

The hydrogen peroxide and water vapour leaving the lead coil and the auxiliary distillation column combine and are introduced into the main column for fractional condensation. This first column is scrubbed with a diluted solution of hydrogen peroxide (approx. 1 to 2 per cent H_2O_2) obtained in the second column. The final product which contains about 35 per cent b. w. H_2O_2 is run off from the bottom of the column and collected in the receiving tourrils.

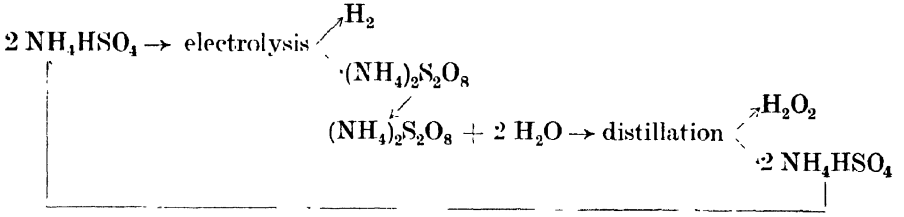
Uncondensed vapour from the first tower is led to the bottom part of the second column which is scrubbed with the condensate obtained from the heating steam which condenses in the distillation equipment. The remaining vapour then leaves the second column and is led to a barometric condenser of standard design connected to a vacuum pump, which maintains a reduced pressure of 110 to 140 mm Hg in the whole distillation equipment and 40 to 60 mm Hg in the condensation. The distillation yield reaches 90 to 92 per cent. A flow sheet is shown in Fig. 140.

Commercial use of the Weissenstein method has been on the whole rather restricted although distillation by this method does not present any particular

technical difficulty and the losses are small. The drawback of the process, however, is the relatively low efficiency of the electrolysis.

b) *The Loewenstein process*

In this process of Schering and Riedel de Haen in Kufstein a solution of ammonium sulphate and sulphuric acid (actually a solution of ammonium hydrogen sulphate) is subjected to electrolysis. The ammonium persulphate thus obtained is hydrolysed, in presence of sulphuric acid, to hydrogen peroxide which is then distilled off. The remaining solution of ammonium hydrogen sulphate is recycled into the electrolytic process. The production cycle is shown in Fig. 141 and the following diagram:



The electrolytic vessel (see Fig. 142) is made of stoneware and built for a load of 750 A. The internal dimensions are 615 × 500 × 520 mm. It is divided by partition *2* into two compartments. Each compartment is divided by diaphragms *3* into two anode spaces *A* and three cathode spaces *B*. In the anode spaces cooling water flows through glass tubes sealed at the bottom.

Eight platinum anodes are suspended in the anode space, having on one side or both sides a foil of smooth platinum *5* (0.05 mm thick, 8 mm wide and 350 mm long). Each foil is welded to platinum wires which are soldered on the copper rods *4* through which the current is conducted to the anode. Against the corrosion effect of the anolyte the copper rods are protected with a coating of rubber. The cathodes made of perforated lead sheets *6* and lead coil *7* to cool the catholyte are placed in the cathode space. Usually the lead coil is welded to the cathodes.

An acid solution of ammonium sulphate enters the cathode spaces in the right section of the cell through openings *8* in the upper part of the tank in three parallel streams. The solution passes through openings *9* at the bottom of the partition into the left section of the electrolyzer and flows through overflow *11* into the next electrolyzer situated below. After the electrolyte has passed through the cathode spaces of all the electrolyzers, it is collected and pumped to the top of the cascade; then it flows through opening *10* into the anode spaces, and enriched with persulphate leaves by overflow *12*.

Double circulation of the solution through the cascade serves the same purpose as in the electrolysis of sulphuric acid, i. e. to remove the residue of Caro's acid and to prevent any permanent change in the composition of the electrolyte.

In this case HSO_4^- and SO_4^{--} ions migrate from the cathode to the anode, whilst H^+ and NH_4^+ ions migrate in the opposite direction. Because only hydrogen ions are discharged at the cathode, the ammonium sulphate content in the catholyte rises while the content of sulphuric acid drops. If, however, this solution after passing through the cathode spaces, is continuously pumped into

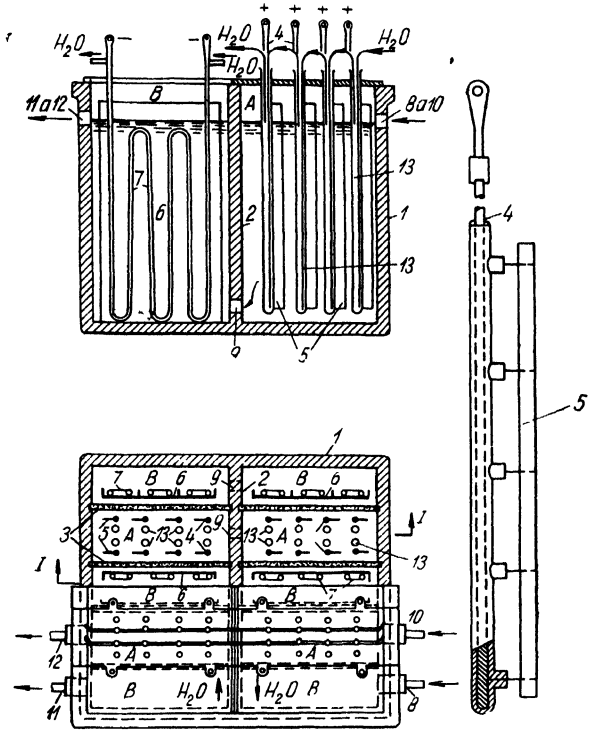


Fig. 142. Electrolyzer for ammonium persulphate production by the Loewenstein method.

A — Anode space, *B* — Cathode space, *1* — Stoneware electrolyzer vessel, *2* — Partitions, *3* — Diaphragm, *4* — Rubber coated copper rod with soldered platinum anodes, *5* — Platinum foil, *6* — Perforated lead sheet cathodes, *7* — Lead cooling coil, *8*, *11* — Catholyte inlet and outlet, *10*, *12* — Anolyte inlet and outlet, *9* — Openings for the electrolyte to flow through the cell, *13* — Cooling pipes in anolyte.

the anode spaces the variation in the concentration previously formed is offset by the migration in the opposite direction so that the electrolyte will regain its original composition.

Current density at the anode reaches 40 to 70 A per sq. dm, and at the cathode 2 to 3 A per sq. dm. Current concentration is approximately 15 to 20 A per

litre. At a temperature of 20 to 25 °C voltage across the bath amounts to 5—5.5 V. Of this total voltage 3—3.5 V is consumed to overcome the anode potential, 0.7 V for the cathode potential and 1.3—1.5 V to surmount the ohmic resistance of the diaphragm and the electrolyte.

The original solution contains 260 to 270 g sulphuric acid and about 230 g ammonium sulphate per litre. While passing through the cathode spaces the effect of the transference of ions will increase the ammonium sulphate content

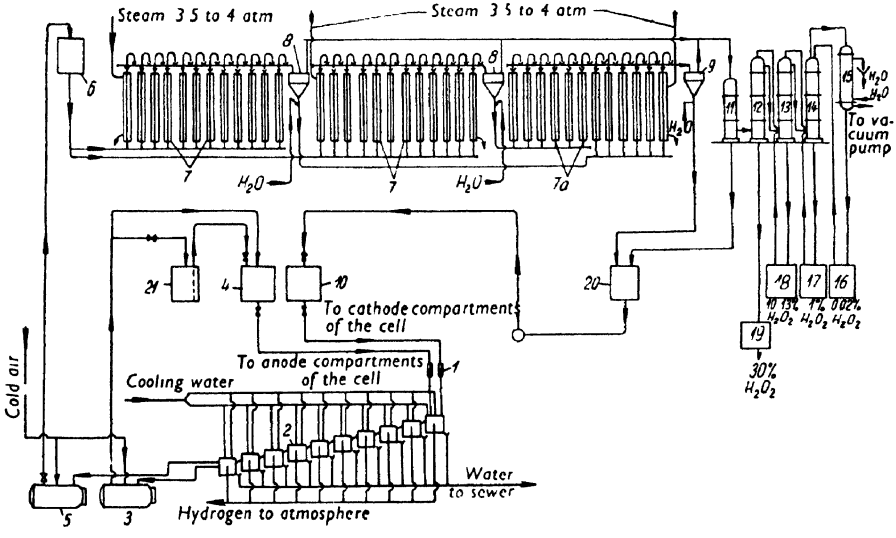


Fig. 143. Flow sheet of the method of producing hydrogen peroxide from ammonium sulphate solutions.

1 — Feeding device, *2* — Electrolytic cells, *3* — Catholyte receiver, *4* — Container for electrolyte which passed through the cathode spaces of the electrolyzer, *5* — anolyte receiver, *6* — Feeding device for ammonium persulphate solution (anolyte) to distillation equipment. *7*, *7a* — Distillation equipment, *8*, *9* — Separators, *10* — Container for returned electrolyte, *11* — Droplets separator, *12*, *13*, *14* — Stoneware fractionating columns, *15* — Aluminium tube condenser, *16*, *17*, *18* — Receivers for individual fractions of hydrogen peroxide, *19* — Receiver for manufactured product, *20* — Reservoir for recycled electrolyte, *21* — Tank for purification of the electrolyte.

to 260 g per litre, while the sulphuric acid content will fall to 220 g per litre. The electrolyte while flowing through the anode spaces is gradually enriched with persulphate (225 to 250 g $(NH_4)_2S_2O_8$ per litre, i. e. 16 to 17.6 g of active oxygen per litre). During the electrolytic process droplets of ammonium thiocyanate solution are added to the anolyte. The current efficiency obtained under these conditions amounts to some 85 per cent. The anolyte is collected into a receiver from where it is led to the distillation system.

The persulphate solution is hydrolysed and distilled at a reduced pressure in two systems of distillation tubes which are parallely connected (see Fig. 143).

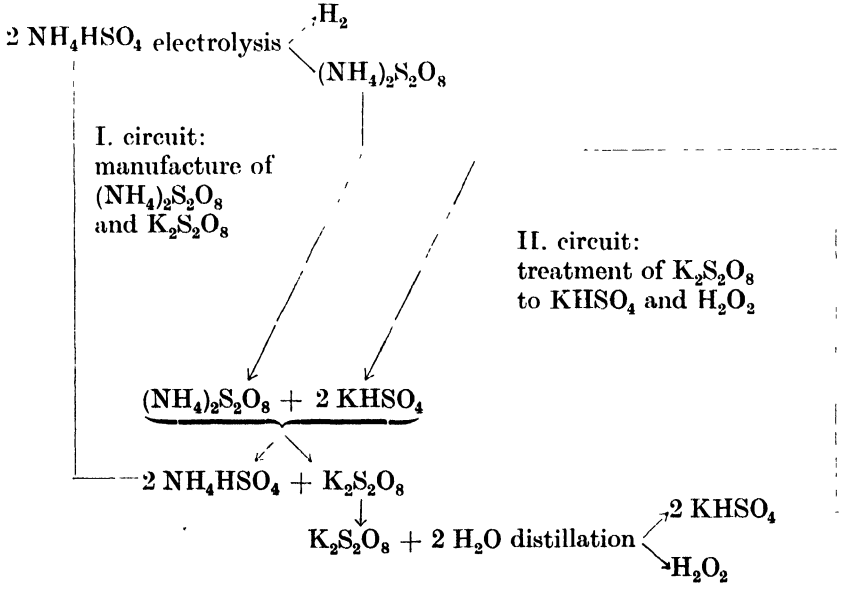
In each system *7* twelve Pyrex or Palex glass tubes or tubes made of antimonia lead are inserted which are 2 600 mm long and 18 mm in internal diameter. The tubes are steel jacketed and heating steam is introduced into the jacket. The tubes are connected at the bottom to a feeding tank, in which a vacuum is maintained equal to that in the distillation tubes. The persulphate solution enters the feeding tank from a receiver through a control cock. The solution in the distillation tubes has the same level as that maintained in the feeding tank and when coming into contact with the hot walls of the tubes is rapidly heated up to boiling point. The liberated vapour of peroxide and water entrain the remaining liquid and drive it along the walls of the tubes at a high velocity which causes the liquid to evaporate still more. The high distillation rate causes the hydrogen peroxide to be separated from the persulphate solution in a very short time. This considerably reduces secondary reactions of the hydrogen peroxide with the persulphuric and Caro's acids which would cause a loss of active oxygen. During the distillation process which proceeds at a temperature between 103 to 105 °C and at a pressure of 110 to 140 mm Hg, about 75 per cent of the total hydrogen peroxide is vaporized. A mixture of the vapour and the remaining liquid leaves at the top of the tubes and is led into stoneware separators *8* where the two phases are separated. The separated liquid is a rather concentrated solution of sulphuric acid and ammonium sulphate which contains approximately one fourth of the original amount of active oxygen, mainly in the form of Caro's acid. In order for further hydrolysis to take place the liquid is diluted with distilled water or with the condensate to the lower concentration necessary and is distilled in a third system which consists of twelve glass tubes *7a*. The mixture of vapour and liquid which leaves at the top of the tubes is separated in a stoneware separator *9*. The remaining liquid which contains less than 10 per cent of the original active oxygen content is diluted with the condensate into a solution similar to the composition of the catholyte and recycled through tanks *20* and *10* into the electrolytic process. The active oxygen which remains in the electrolyte in the form of Caro's acid is removed by reduction when passing through the cathode spaces of the cells. Heavy metals, particularly copper are deposited on the cathode which prevent the persulphate decomposing and reducing the yield during electrolysis and distillation.

Water and hydrogen peroxide vapours from the first and second distillation system are combined and pass through stoneware tower *11* where the residue of the entrained sulphuric acid is separated by a packing of Raschig rings. These residues run into container 20 and from there into the electrolytic process. The vapours are then led into three stoneware fractionating columns *12*, *13* and *14* which are connected in series and also packed with Rachig rings. Here, at a reduced pressure of 35 to 45 mm Hg, fractional condensation occurs so that in the first column the most concentrated peroxide is obtained, in the last the weakest. Uncondensed vapour is led through a water cooled aluminium tube condenser *15* where it condenses. At the end of the system a suitable vacuum

pump is attached, which maintains the vacuum required throughout the whole distillation and condensation system. The condensates from columns *13*, *14* and from the condenser *15* are led by barometric legs into receivers *16*, *17* and *18*. Vacuum tourills are sometimes used instead of barometric legs and seals. A portion of the condensate from the aluminium condenser which contains 0.02 per cent b. w. H_2O_2 is pumped from receiver *16* to the top of column *14*. The condensate from the latter column, containing about 1 per cent b. w. H_2O_2 flows into a receiver *17*, and is used to scrub column *13*. Finally, the condensate from receiver *18* which contains 10 to 13 per cent b. w. H_2O_2 is introduced into the first column *12*. In this way the mixture of water vapour and hydrogen peroxide passes through individual columns, countercurrently to the condensate. From column *12* the condensate which contains 30 to 35 per cent b. w. H_2O_2 is led to receiver *19* as the manufactured product. The distillation yield will vary between 80 to 90 per cent according to the degree of purity of the electrolyte.

In order to remove the catalytically active iron salts, a portion of the circulating electrolyte is periodically removed, after having passed through the cathode spaces to get rid of active oxygen. Iron is precipitated by potassium ferrocyanide and the Prussian blue deposit is filtered off by a suction filter. The purified electrolyte is then returned to normal circulation.

The equipment necessary for the Loewenstein method is somewhat simpler than that of the Adolph-Pietsch method; therefore, it is more suitable for medium sized plants. In comparison with the Weissenstein method, the Loewenstein process gives somewhat higher yields.



e) *Adolph-Pietsch process*

This method, which was worked out by the Electrochemische Werke in Munich, is similar to the Loewenstein method. In the first stage of the electrolytic process which starts with ammonium hydrogen sulphate ammonium persulphate solution is obtained. When reacting with potassium hydrogen sulphate, this intermediary product is converted to a slightly soluble potassium per-

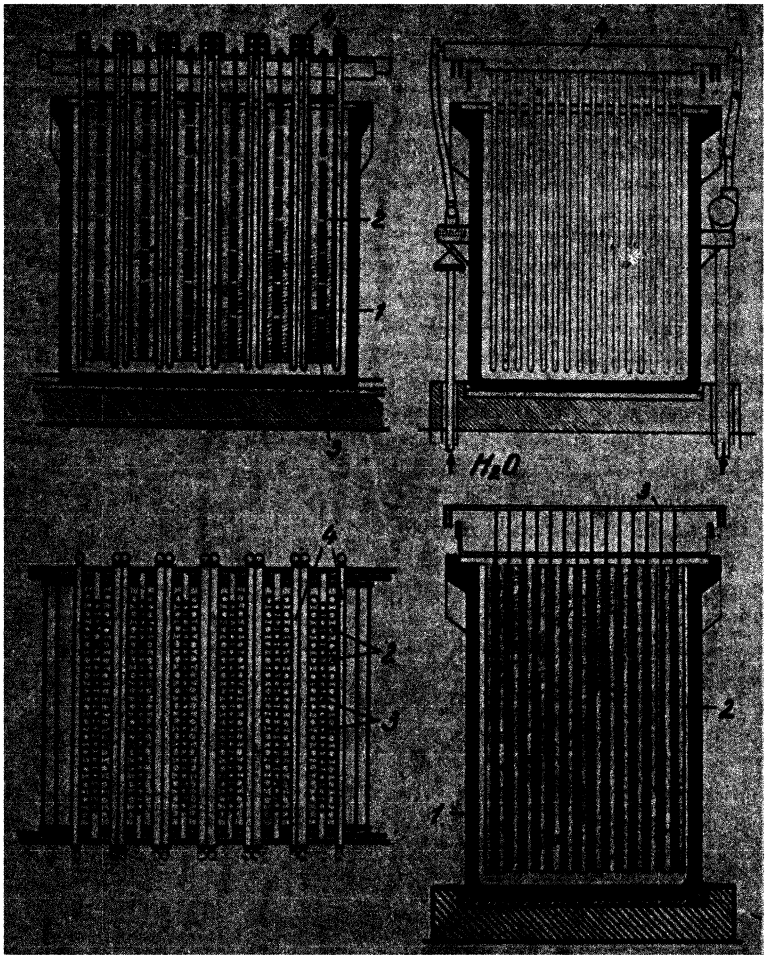


Fig. 144. Electrolyzers for the manufacture of ammonium persulphate according to Adolph and Pietsch.

1 — Stoneware tank, *2* — Cathodes, *3* — Anodes, *4* — Cooling.

sulphate which is then decomposed by live steam in the presence of sulphuric acid and the liberated hydrogen peroxide is distilled off at a reduced pressure. The remaining potassium hydrogen sulphate is recirculated into the conversion process. The overall process, therefore, consists of two closed circuits, which are represented by the diagram shown in p. 409.

a) Ammonium persulphate circuit

An ammonium hydrogen sulphate solution is electrolyzed in a number of cells connected in series and arranged in cascades. A stoneware tank (see Fig. 144) of an individual electrolyzer (built for a load of 4500 A) has internal dimensions 940 × 780 × 875 mm. Each electrolytic unit has six sets of electrodes, each set consisting of 14 anodes; on both sides of the anodes there are 15 graphite cathodes. Placed behind each row of cathodes are 16 glass coolers.

The anodes (see Fig. 145) consist of aluminium rod with platinum side arms on which platinum wires are arranged in 8 turns. The aluminium support is thoroughly coated with rubber. Current density at the anode varies between 100 to 150 A per sq. dm. (In war-time Germany current density was increased to 200 A per sq. dm. because of the shortage of platinum).

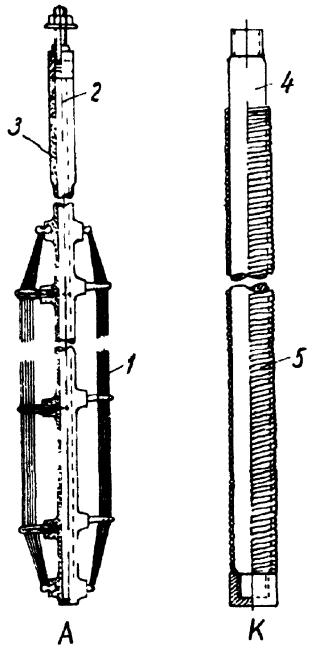


Fig. 145. Anode and cathode of the cell according to Adolph and Pietsch.

A — Anode, *1* — Platinum wire, *2* — Aluminium stem, *3* — Rubber lining, *B* — Cathode, *4* — Graphite rod, *5* — Diaphragm of asbestos cord.

The cathodes are graphite rods round which an asbestos cord is wound which acts as a diaphragm. The cathodes are screwed into graphite plates which also serve as a cover to the cell. In order to prevent the formation of free ammonia current density at the cathode is kept low, approximately 4 A per sq. dm. Hydrogen accumulating under the cover is removed by a stream of air, which dilutes the hydrogen and keeps it at a concentration below 5 per cent. The coolers are glass tubes which are closed at the bottom and provided with inner tubes for introducing the cooling water.

The voltage in the bath varies from 5.5 to 6.5 V, current concentration equals some 15 A per l., whilst current efficiency reaches some 85 per cent.

The solution on leaving the centrifuges, where the poorly soluble potassium persulphate has been separated, is introduced into the electrolyzers, after the Caro's acid which remained in it from the previous operation had been reduced by treating with sulphur dioxide. This solution, entering the cells at 18 °C,

contains about 300 g $(NH_4)_2SO_4$, 40 g K_2SO_4, 60 to 80 g H_2SO_4 and about 5 g of active oxygen per litre, the latter in the form of persulphate which cannot be reduced by sulphur dioxide. The solution on leaving the electrolyzer at a temperature of 38 °C, has about twice the content of persulphate. In view of this comparatively low content of the active oxygen in the final solution, the reduction of $S_2O_8^{--}$ ions can be satisfactorily avoided if the cathodes are wrapped in asbestos.

The electrolyte, enriched with persulphate, is first filtered in order to remove the graphite, asbestos etc. Then it is cooled in a vacuum cooler to 28 °C and finally introduced into a converter of stainless steel, which has a stirrer and a cooling jacket. Here at a temperature of 15 °C, after solid potassium hydrogen sulphate has been added, the following reaction takes place:

$$(NH_4)_2S_2O_8 + 2\,KHSO_4 = K_2S_2O_8 + 2\,NH_4HSO_4. \qquad (XX\text{-}30)$$

Conversion is carried out in such a manner that only about a half of the ammonium persulphate present is converted to the slightly soluble potassium salt, the remainder is recycled into the electrolytic process. (Not more than a half of the persulphate should be converted, otherwise too much potassium salt would pass into the solution. During electrolysis this would be separated in the form of a poorly soluble potassium persulphate and obstruct the process). Potassium persulphate crystals are separated from the solution by stainless steel centrifuges.

In order to avoid an accumulation of iron compounds (max 50 mg. Fe per litre) a certain portion of the circulating liquid is led into spacious precipitating tanks where it is neutralized by gaseous ammonia. The precipitated ferric hydroxide is allowed to settle and the clear solution is siphoned and boiled down. The separated crystals of pure ammonium sulphate are centrifuged and recycled into the electrolytic process.

b) *Potassium persulphate circuit*

Crystals of potassium persulphate are hydrolysed by the action of direct steam in the presence of sulphuric acid (50 °Bé):

$$K_2S_2O_8 + 2\,H_2O + (H_2SO_4) = 2\,KHSO_4 + H_2O_2 + (H_2SO_4). \qquad (XX\text{-}31)$$

According to the above equation, the acid acts as a catalyst carrying over the peroxide oxygen to water. While the peroxide is being distilled, more steam is introduced, so that the concentration of sulphuric acid remains constant during the whole hydrolysis. In the presence of a permanent excess of potassium persulphate a concentrated solution of hydrogen peroxide is formed by hydrolysis in the distillation retort and vapours rich in hydrogen peroxide are obtained, which, compared to the previously described methods, contains on an average 8 to 10 per cent b. w. H_2O_2. The main advantage of the Adolph-Pietsch method is that pure potassium persulphate is used for hydrolysis, as during conversion

of ammonium salt with potassium hydrogen sulphate all the impurities that might catalyze the decomposition of hydrogen peroxide during distillation (e. g. Fe, Mn, Pt) remain in the mother liquor.

Hydrolysis together with the distillation and the fractional condensation is carried out at a reduced pressure in the apparatus shown in Fig. 146.

Potassium persulphate is introduced into a stoneware retort which has also a sulphuric acid inlet. Three porcelain pipes introduce the steam into the mass

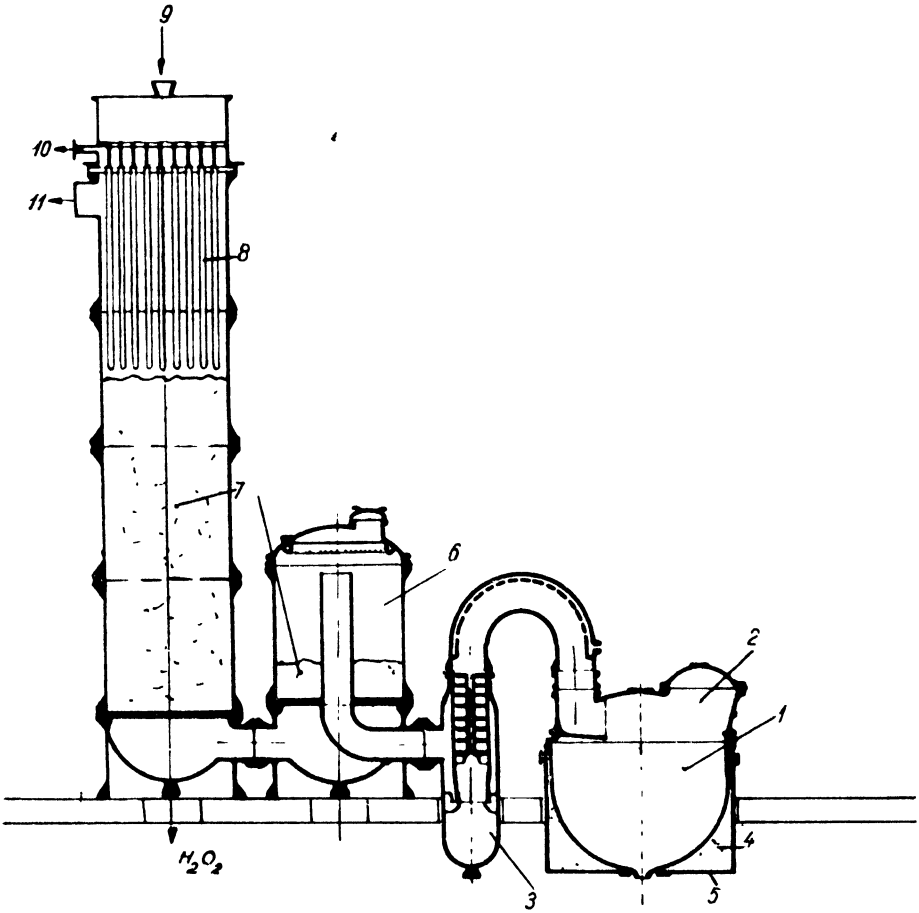


Fig. 146. Distillation equipment for the manufacture of hydrogen peroxide according to Adolph and Pietsch.

1 — Distillation retort, *2* — Feeding opening for potassium persulphate, *3* — Droplets separator, *4* — Insulation of the retort, *5* — Steel jacket, *6* — Separator of entrained droplets, *7* — Porcelain rings, *8* — Dephlegmator, *9* — Cooling water inlet, *10* — Cooling water outlet, *11* — Water vapour offtake to aluminium condenser.

of crystals. It is unnecessary to externally heat the retort because the heat content of the steam and the reaction heat evolved will maintain the temperature necessary for the distillation. Distillation which is carried out at a reduced pressure of 50 mm Hg and at a temperature of 80 °C, is an easy process and not so sensitive as distillation in the Loewenstein process. Hydrogen peroxide and water vapour is passed through a stoneware droplets separator and a low tower packed with Raschig rings, in which the entrained mist of sulphuric acid is separated. The separated sulphuric acid is drained off from the bottom of these apparatuses, while the vapour passes, through a side tube, into the bottom part of the rectifying column, which is 1100 mm in diameter and 5800 mm high. Due to a high hydrogen peroxide content in the vapour one column only is used which is packed with Raschig rings. A dephlegmator is attached to the column, through which cooling water passes. In it a certain portion of the vapour (chiefly the remaining H_2O_2) will be condensed and used as a reflux for the satisfactory rectification of the vapour mixture H_2O_2 — H_2O. Condensed hydrogen peroxide, the average concentration of which amounts to 35 % b. w. H_2O_2 (at the beginning of distillation a 50 per cent H_2O_2 solution is condensed and towards the end a 20 per cent solution), is drained off from the bottom of the column. The uncondensed vapour containing a negligible percentage of peroxide is led by a side tube from the dephlegmator into an aluminium water cooled tube condenser. A vacuum pump is also connected to the apparatus in order to maintain in the condenser an absolute pressure of about 30 mm Hg. Pressure difference between the condenser and the retort amounts to 20 mm Hg. Distillation yields, on an average are 90 to 94 per cent, which is very satisfactory. Distillation is carried out in batches, the treatment of one batch of 1100 kg $K_2S_2O_8$ takes $4^1/_2$ hours under normal conditions. In another modification of the process it is possible to hydrolyze and distil potassium persulphate continually.

The sludge of potassium hydrogen sulphate and sulphuric acid remaining in the retort is first cooled to 18 °C in an austenitic steel cooler and then separated in a centrifuge made of the same material. The potassium hydrogen sulphate crystals are returned to the process to convert the ammonium persulphate. The separated sulphuric acid which has a concentration of about 40 per cent still contains a small amount of active oxygen (in the form of H_2O_2 and H_2SO_5) and impurities such as iron and platinum. After dilution with water, the remaining Caro's acid and hydrogen peroxide are first reduced by sulphur dioxide and iron is precipitated by potassium ferrocyanide. The precipitated Prussian blue is filtered off by ceramic candle filters and the purified sulphuric acid, containing less than 5 mg Fe per litre, is boiled down at a reduced pressure of 50 to 60 mm Hg. to a 50 °Bé concentrated acid and then returned into the retort. A coil made of an alloy containing 70 per cent gold and 30 per cent silver is used to heat the sulphuric acid in the course of evaporation. Steam of 4 atm. pressure is introduced into the coil. The filtered off Prussian blue which contains platinum, is transported to a precious metal refinery.

The Adolph-Pietsch process is more complicated than other methods, but it gives a very pure, acid-free product at comparatively very high yields. Due to the complicated machinery and the great number of operations this method is only suitable for high capacity plants where the high yield and the better quality of the hydrogen peroxide obtained will pay for the higher initial and production cost.

Energy requirement and other data related to the production of 1 kg of 100 per cent H_2O_2 by all methods described are indicated in Table 19.

Table 19. Energy consumption and yields in hydrogen peroxide manufacture

	Weissenstein	Loewenstein-Riedel	Pietsch-Adolph
Direct current for the electrolysis	15.9 kw–hr	13.0 kw–hr.	13.0 kw–hr.
Alternating current for the electrolysis	17.1 kw–hr.	14.0 kw–hr.	14.0 kw–hr.
Total alternating current including auxiliary current	19.0 kw–hr.	–	17.6 kw–hr.
Steam	28.6 kg.	44.0 kg.	25.0 kg.
Current efficiency	70–78 %	85 %	85 %
Distillation yields	90–92 %	83–87 %	92–94 %
Total efficiency*)	65 %	72 %	78 %
Platinum loss	1.2. 10^{-6}g/A-hr.	–	1.0. 10^{-6}g/A-hr.

*) Total efficiency is the product of current efficiency and distillation yield.

E. STABILIZATION OF HYDROGEN PEROXIDE

Maximum stability of hydrogen peroxide would be attained, if no impurities at all would have entered during manufacture or storage. As, however, all products contain impurities, depending on the production method used, certain substances must be added to improve the stability of the peroxide.

In view of the great number of substances which act as catalysts accelerating the decomposition of the hydrogen peroxide, it is not surprising that a very large number of stabilizers is known.

The efficiency of these negative catalysts or inhibitors depends first of all on the amount of impurities contained in the hydrogen peroxide. If impurities are few the solution can be stabilized for a long time. If considerable amounts of impurities are present the addition of stabilizers has no effect. It is, therefore, preferable to redistil the product.

Apart from this, the efficiency of the stabilizers depends on the pH of the solution. Commercial grades of hydrogen peroxide which must be stored for a long time are adjusted to achieve a slightly acid reaction (pH = 2—5), at which

hydrogen peroxide is very little dissociated. Higher acidity will unfavourably influence the stability and is prohibited for certain uses. Hydrogen peroxide is more stable the more concentrated the solution, for the number of associated $(H_2O_2)_n$ molecules which represent a stable formation is increased with concentration. Pure anhydrous hydrogen peroxide, however, is stable only at a temperature below 0 °C.

It is assumed that inhibitors precipitate the compounds which catalyze the decomposition of hydrogen peroxide or form complexes with them. Phosphoric acid, meta-, ortho- and pyro-phosphates, salicylic and benzoic acids, oxyquinoline etc. belong to this group of inhibitons. The efficiency of inorganic and organic colloids such as tin dioxide, magnesium silicate, dextrine etc. is accounted for by their ability to adsorb catalysts. It is also probable that anticatalytic agents break the chain reaction by which, according to recent concepts hydrogen peroxide is decomposed.

Substances which are employed to stabilize hydrogen peroxide for a long period of storage are divided according to their nature into inorganic acids, inorganic salts and organic compounds. Industrially it is usual to add several different stabilizers at the same time as the total efficiency of the mixture by far exceeds the sum of the efficiency of all the individual stabilizers.

Sulphuric, phosphoric and pyrophosphoric acids are among the inorganic acids particularly recommended. Actually it is unnecessary to add sulphuric acid, as the final product usually contains an excess of this acid which must be neutralized by alkaline reacting substances. Experience has also shown that mere acidification of peroxide solutions does not ensures sufficient stability of the product, moreover a greater smount of acid in pharmaceutical product is prohibited.

Sodium pyrophosphate ($Na_4P_2O_7 \cdot 10\,H_2O$) is the most popular of the inorganic salts. It also acts as an agent to neutralize sulphuric acid if it is present in the solution in a notable amount.

Among the great number of organic compounds known as stabilizers the following must be mentioned: benzoic, salicylic, acetic and hippuric acids, phenacetin, naphtalene, oxalic acid, acetamide, urea etc. A combination of sodium pyrophosphate (0.5 to 1 g per 1.) and benzoic or sylicylic acid (0.4 g per 1.) is frequently used. This has particularly good results with peroxide for technical purposes. In pharmaceutical products the amount of pyrophosphate added is reduced and the amount of benzoic acid increased. For other purposes hippuric acid (1 g per 1.) with a slight admixture of phosphoric acid is used as stabilizer. Perhydrol is the peroxide used for analytical purposes. It is redistilled three times in order to remove any impurities. This product requires no stabilizer.

A special group of inhibitors are those substances which suppress the decomposition of hydrogen peroxide in alkaline solutions, which are used for bleaching purposes or for preparation of addition compounds of hydrogen peroxide. Good stabilizers for such solutions are e. g. magnesium orthosilicate, water glass and phosphates of alkaline-earth metals.

F. MANUFACTURE OF HYDROGEN PEROXIDE CONTAINING 80 TO 85 PER CENT B. W. OF H_2O_2

By double distillation and fractional condensation of peroxide which contains 30 to 35 per cent b. w. H_2O_2,a product is obtained containing 80 to 85 per cent b. w. H_2O_2. If peroxide is manufactured which contains more than 87 per cent H_2O_2 spontaneous decomposition sets in during distillation so that 85 per cent should be considered the limit concentration for the technical product, which possibly cannot be exceeded on an industrial scale.

Hydrogen peroxide containing 30 to 35 per cent b.w. H_2O_2, manufactured by one of the electrochemical methods described, is as a rule not sufficiently pure for further concentration to 80—85 per cent b.w. Therefore, it is usually re-distilled, stabilized by an admixture of sodium pyrophosphate (or 8-hydroxyquinoline), and eventually filtered by passing through a tower packed with Raschig rings.

Concentration to a product containing 80 to 85 per cent b. w. H_2O_2 proceeds in two stages. In the first stage the peroxide is concentrated to a 65 per cent intermediary product which in the second stage is redistilled to obtain 80 to 85 per cent b. w. H_2O_2. The operation is carried out in two identical distillation units in series. Each consists of a retort, an acid separator and a rectifying column with a dephlegmator and a water vapour surface condenser (see Fig. 147).

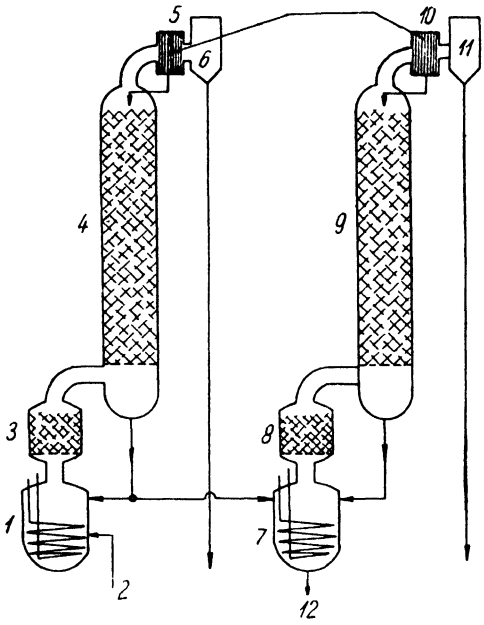


Fig. 147. Apparatus for the manufacture of 80 to 85 per cent hydrogen peroxide.

1 — First retort, *2* — 30 to 40 per cent b. w. H_2O_2 peroxide inlet, *3* — Droplets separator, *4* — Rectifying column, *5* — Dephlegmator, *6* — Condenser, *7* — Second retort, *8* — Separator, *9* — Rectifying column, *10* — Dephlegmator, *11* — Condenser, *12* — 80 per cent b. w. H_2O_2 peroxide outlet.

A stabilized and purified solution of 30 to 35 per cent b. w. H_2O_2 enters the stoneware retort of the first distillation system at a rate of 700 litres per hour. This is heated by a steam coil made of special Ni-Cr-Mo steel to 66 °C, under 45 mm Hg. absolute pressure. The distilled vapour first passes through a separator, packed with Raschig rings, and afterwards enters a stoneware

rectifying column which is also filled with rings and combined with a water cooled aluminium dephlegmator. Water vapour which leaves the dephlegmator is condensed in an aluminium tube condenser connected to a vacuum pump. At the beginning of the operation condensed liquor from the rectifying column is returned to the retort until the concentration of the solution in the retort reaches approximately 73 per cent b.w. H_2O_2. At the same time the equilibrium concentration of H_2O_2 at 66 °C in the vapour phase is about 30 p. c. b. w. which corresponds to the composition of the feed. When this state is reached the connection between the column and the first retort will be interrupted and the condensate from the column which contains about 65 per cent b.w. of H_2O_2 is allowed first to pass through a long glass cooler, which is cooled externally by water to 25—30 °C, and then into the second retort. During the distillation process all the impurities contained in the initial peroxide solution remain in the first retort and this is the reason for the stability of high percentage product. The process taking place in the first apparatus is stopped as soon as the content of solids in the solution in the retort has reached 50 g per litre, i. e. after about 4 to 5 days. This solution is drained off from the retort and the hydrogen peroxide in it is expelled by direct steam in a special distillation equipment at a reduced pressure of 40 mm Hg. The hydrogen peroxide recovered in this way is a pure solution containing around 35 per cent b.w. H_2O_2, which is returned into the process.

The 65 per cent peroxide, previously stabilized by adding a small amount of phosphoric acid, is introduced at the rate of 900 l per hr. into a second distillation unit, similar to the first, for re-distillation. Here the process is continuous as no solid substances accumulate in the retort. A temperature of 75 °C is maintained at an absolute pressure of 40 mm Hg. When equilibrium has been reached, the concentration of the liquid in the retort will be about 80 per cent b.w. H_2O_2 and in the vapour phase will be about 44 per cent b.w. H_2O_2. The distilled vapour enters the rectifying column, from where a condensate containing 56 per cent b.w. H_2O_2 is continually returned into the retort. Uncondensed water vapour is liquefied in a tubular aluminium condenser connected to a vacuum pump.

The final product is drained off from the retort, cooled and stored in aluminium tanks in which, if necessary, it is stabilized with phosphoric acid, pyrophosphate and 8-hydroxyquinoline. The stability of hydrogen peroxide with a high percentage is very high. After being stored a year in aluminium tanks it loses hardly more than 0.5 to 1 per cent of active oxygen. In view of this, it is also suitable for shipment to tropical countries.

80 to 85 per cent hydrogen peroxide is an almost colourless liquid with specific gravity of 1.35. Care must be taken to prevent it from coming into contact with clothing, skin, wood or oil. In case the temperature of such a solution begins to rise spontaneously and peroxide starts to decompose it must be diluted with water or the container in which the peroxide is kept must be cooled externally. Concentrated peroxide contains a great amount of oxygen. As it is

a strongly endothermic compound it releases a great amount of heat when decomposing. Decomposition of 1 litre of 90 per cent H_2O_2 will yield a mixture of 589 g oxygen and 801 g water vapour. If the decomposition is performed adiabatically the resulting mixture will reach a theoretical temperature of 750 °C with a volume amounting to 5000 litres at a pressure of 1 atm. Spontaneous decomposition is very slow when hydrogen peroxide is protected from the effect of heat, light and dust. To initiate decomposition, solid catalysts are used (such as manganese dioxide) or liquid ones, such as, permanganate solution or porous substances impregnated with suitable solutions.

G. USE OF HYDROGEN PEROXIDE

The concentration of hydrogen peroxide is stated either in per cent by weight (i. e. by the number of grams of H_2O_2 in 100 g of the solution), or else in per cent by volume (i. e. grams of H_2O_2 in 100 cu. cm. of the solution). A product containing 27.2 per cent H_2O_2 by weight is equivalent to peroxide containing 30 per cent H_2O_2 by volume, a product containing 30 per cent H_2O_2 by weight is equivalent to peroxide containing 33.33 per cent H_2O_2 by volume, whilst a product containing 35.2 per cent H_2O_2 by weight is equivalent to peroxide containing 40 per cent H_2O_2 by volume.

The customary commercial products are: Hydrogen peroxide for technical purposes containing 30 p. c. or 40 p. c. by volume and pharmaceutical peroxide containing 30 p. c. H_2O_2 by weight.

Technical hydrogen peroxide which contains 30 to 40 p. c. H_2O_2 by volume is shipped in glass carboys or aluminium tank cars. Pharmaceutical product is shipped in glass carboys while the chemically pure product is packed in small bottles which are lined with paraffin and closed with paraffin stoppers.

A 30 or 40 per cent by volume hydrogen peroxide is used as bleach for silk, wood, wool, bones, teeths, feathers, mother of pearl, horn, hair, coral, gelatine, oils and fats. In medical science it is an excellent disinfectant and is also essential for sterilizing water for municipal use and preserving milk. Apart from this, hydrogen peroxide is used in the chemical industries for the manufacture of persalts and in laboratories for oxidation.

Commercially, also solid hydrogen peroxide (perhydrite) containing 34.5 per cent H_2O_2 is used. It is an addition compound with urea and contains hippuric as well as citric acid as stabilizers.

On the world market an 80 to 85 per cent H_2O_2 is sold in an increasing rate and preferred because its transport is cheaper. In Germany, large plants such as Bad Lauterberg plant with a monthly capacity of 1 200 tons of 100 p. c. H_2O_2 and Rhumspringe plant with a capacity of 1 800 tons of the same product, were built during the war to manufacture this product for war purposes.

The latent energy of the peroxide was used to propel the V-1 and V-2 rockets. As an efficient accumulator of oxygen it was also used for the combustion of fuels (tetrahydronaphtalene or a mixture of methanol and hydrazine hydrate)

to drive torpedoes and submarine turbines. By solving the problem of manufacture, storage, and transport of hydrogen peroxide, further opportunities have been opened for it to be used on a wide commercial scale. The outstanding properties as the low specific gravity, liquid state, the ability to free all peroxide oxygen, remarkable oxidation power and the high oxygen content have predetermined hydrogen peroxide as the ideal oxidizing agent of the future.

In Czechoslovakia, technical and pharmaceutical hydrogen peroxide is manufactured according to Government standards. The specifications are quoted in Table 20:

Table 20.

	Pharmaceutical product.		Technical product
	Grade *A* per cent b. w.	Grade *B* per cent b. w.	Grade *C* per cent b. w.
H_2O_2	28–32	32–35,5	27–31
Free H_2SO_4 max.	0.1	0.2	0.2
Residue from evaporation max.	0.1	0.2	0.2
Residue on ignition max.	0.1	0.1	0.1

XXI. SODIUM PERBORATE

True perborates are e. g. the compounds $KBO_3 . 0.5 H_2O$, $NH_4BO_3 . 0.5 H_2O$ and $NaBO_3$; these substances are, however, not marketed as their manufacture is too expensive. The compound which is incorrectly known on the market as sodium perborate is really an addition compound of metaborate and hydrogen peroxide, the formula of which corresponds to sodium metaborate-perhydrate $NaBO_2 . H_2O_2 . 3 H_2O$. This substance is a white crystalline powder which is but poorly soluble in water. Due to hydrolysis this solution has a weak alkaline reaction and behaves chemically as hydrogen peroxide. At a temperature between 50 and 60 °C it starts to decompose and liberate oxygen; at 100 °C this decomposition is already violent. With diluted acids perborate yields hydrogen peroxide. When treated with concentrated sulphuric acid it decomposes and liberates oxygen and ozone. It is also decomposed by other substances, e. g. lead dioxide, manganese dioxide, potassium permanganate, silver nitrate, platinum black, cupric oxide, cobaltous oxide etc. It is evident from the chemical formula, that perborate contains theoretically 10.38 % active oxygen. If dry and pure and not contaminated with substances promoting catalytic decomposition this compound is very stable; if stored in open containers it loses 0.1 % of active oxygen within a year's period, and about 0.2 % during two years.

If the water is displaced from the perborate by the action of hydrogen peroxide it is possible to increase the content of active oxygen in the product up to about 30 %; but such products are not sufficiently stable. A more stable product containing up to 20% of active oxygen can be prepared by dehydration of the compound $NaBO_2 . H_2O_2 . 3 H_2O$ over sulphuric acid, or phosphorus pentoxide, or by drying under reduced pressure at a maximum temperature of 50 °C.

A. RAW MATERIALS FOR THE MANUFACTURE OF SODIUM PERBORATE

Boric acid H_3BO_3 (sasoline) or sodium tetraborate $Na_2B_4O_7 . 10 H_2O$ are used as row materials for the manufacture of sodium perborate according to the character of the manufacturing process, which may be chemical or electrochemical.

1. Boric acid

Boric acid escapes with jets of steam called soffioni from the ground in central Tuscany in Italy. Steam with a pressure of 3 atm. and 190 °C, which contains around 0.1 % of boric acid, is first utilized in a steam turbine and then to concentrate the liquors; afterwards it is condensed in water basins to a solu-

tion containing about 2 per cent H_3BO_3. After the sludge has been separated the solution is boiled down in vacuum evaporators; the concentrated solution from which the gypsum has been separated by settling is allowed to crystallize. The raw boric acid is refined by re-crystallisation.

The mineral boronatrocalcite i. e. double borate of sodium and calcium $Na_2O \cdot 2\,CaO \cdot 5\,B_2O_3 \cdot 16\,H_2O$, is found mainly in Chile and Peru. It is decomposed with diluted hydrochloric acid in wooden vats and boric acid is obtained by crystallizing from clear leach liquor. In a similar way is also treated the mineral boracite which is mainly magnesium borate and chloride $MgCl_2 \cdot 5\,MgO \cdot 7\,B_2O_3$ and is found at Stassfurt. Pandermite calcium borate $2\,CaO \cdot 3\,B_2O_3 \cdot 3\,H_2O$, the most important deposits of which are in Anatolia, is processed to boric acid by treatment with sulphuric acid. In USSR the minerals ascharite $2\,MgO \cdot B_2O_3 \cdot H_2O$ and hydroboracite $CaO \cdot MgO \cdot 3\,B_2O_3 \cdot 6\,H_2O$ are used as raw materials to manufacture boric acid. They are decomposed at 80 to 90 °C by sulphuric acid; the solution is separated from the insoluble residue by filtration on vacuum filters. On cooling the solution in crystallizers the crystals of crude boric acid are separated which are afterwards refined by re-crystallisation.

2. Sodium tetraborate

Sodium tetraborate $Na_2B_4O_7 \cdot 10\,H_2O$ known as mineral tinkal (natural borax) is found on the shores of certain lakes in Tibet and East Indies. These deposits were formerly exploited and the pure salt was obtained by crystallizing from the hot solution.

Many methods are used to manufacture synthetic borax. First of all it is possible to manufacture borax if boric acid is gradually introduced into a solution of soda at 90 to 100 °C. After settling and separating insoluble substances by filtration, the solution is cooled in a crystallizer, in order to separate the crystals which are finally centrifuged. The mother liquor is used to dissolve new charges of soda ash.

Borax can be prepared from mineral boronatrocalcite by the following method: the finely ground mineral is decomposed in a boiling solution to which soda ash and the sodium hydrogen carborate are successively added in proportion so that the following reaction takes place:

$$2\,Na_2O \cdot 2\,CaO \cdot 5\,B_2O_3 \cdot 16\,H_2O + 2\,Na_2CO_3 + 2\,NaHCO_3 = 5\,Na_2B_4O_7 + 4\,CaCO_3 + 33\,H_2O. \qquad \text{(XXI-1)}$$

The reaction proceeds in two stages. In the first stage the reaction components are heated by direct or indirect steam in wooden vats which are lined with lead and provided with stirrers. A small quantity of bleaching powder is added to oxidize and precipitate the iron. The insoluble residue separated by filtration of the solution is still containing a certain quantity of boric oxide; it is, therefore, charged into an autoclave with a stirrer, where after the addition of a fresh

solution of soda and sodium hydrogen carbonate it is heated to 120—130 °C at 2—3 atm. The second filtrate is filtered on a filter-press and added to the first. The hot solution is afterwards pumped into a crystallizer where the borax crystallizes after cooling bellow 56 °C (at a temperature above 56 °C the octahydrate crystallizes instead of decahydrate). After the first product has been separated the mother liquor is concentrated in a vacuum evaporator and allowed to crystallize to obtain the second product. The leaching of pandermite with soda and hydrogen carbonate must be also carried out at a high temperature and at a pressure of 2—4 atm.

The mineral rasorite (kernite), tetrahydrate of sodium tetraborate is a very suitable material for the production of borax. Its formula is $Na_2B_4O_7 . 4 H_2O$. Deposits are found in California. As rasorite is comparatively a very pure raw material, containing only about 5 % of impurities (Al_3O_3, Fe_2O_3, MgO, CaO), it is very easy to process it to borax for technical purposes.

Rasorite is dissolved at 90 °C in mother liquor in a tank equipped with an agitator and a heating coil. Iron is oxidized during this process by bleaching powder, and a small amount of soda ash is added in order to improve crystallization. The solution then passes through a filter-press and is diluted with mother liquor in order to reduce the temperature below 56 °C. After this, it is cooled in a crystallizer to 30 °C whereby tetraborate crystallizes out. The mother liquor is then removed from the crystals on a centrifuge. After washing with water the crystals are dryed by air, with a maximum temperature of 50 °C in order to avoid the loss of water of crystallisation. The mother liquor is recirculated to dissolve more rasorite after the silicic acid had been removed from it by precipitation with sodium aluminate and filtration.

If the borax obtained is used to manufacture perborate by the electrolytic method it is necessary to carefully remove all impurities, such as the salts of heavy metals (Fe, Mn), silicic acid and any remaining quantity of organic substances which reduce the current efficiency of the electrolysis and decrease the stability of the product. Rasorite is therefore dissolved in mother liquor, filtered, and bleaching powder is added to the clean solution together with perborate in order to oxidize the organic substances; simultaneously, fresh precipitated ferric hydroxide is added, in order to entrain the salts of heavy metals into the sediment. The solution is filtered again and from the filtrate borax is crystallized; before the mother liquor is recirculated to further dissolution of the rasorite it is again purified with sodium aluminate, ferric hydroxide, and if necessary, with bleaching powder and filtered.

Borax is used in the glass industry (chemical and optical glass, lamp cylinders, artificial precious stones), for enameling metals and to manufacture enamels in ceramic industries (stoneware, porcelain etc.) as well as in chemical industry to prepare borates, sicatives and perborates. To a smaller extent it is used in laundries, for soldering and melting metals, to produce putty, as a fireproof agent to impregnate wood and fabrics, for medicinal and cosmetic purposes and as admixture to fertillizers.

B. CHEMICAL METHODS OF MANUFACTURING SODIUM PERBORATE

If hydrogen peroxide reacts with a solution of sodium tetraborate in an alkaline medium, sodium perborate is formed according to equation:

$$Na_2B_4O_7 \cdot 10\,H_2O + 4\,H_2O_2 + 2\,NaOH + H_2O = \\ = 4\,NaBO_2 \cdot H_2O_2 \cdot 3\,H_2O. \qquad \text{(XXI-2)}$$

Soda ash can be used instead of sodium hydroxide. This process is carried out in wooden or iron vessels, lined with tiles and equipped with a wooden stirrer as well as lead or tin plated steel coil through which an aqueous solution of glycerine flows which has previously been chilled to about — 5 °C in an ammonia cooling equipment.

The vessel is first filled with a solution of sodium hydroxide (11 g. NaOH per litre), borax is then added and the whole content cooled to + 15 °C. Afterwards a small quantity of suspension of magnesium silicate*) (so called milk of silicate) is added, to suppress the effect of catalytically acting substances which can reduce the stability of the product. Finally a 20—40 per cent hydrogen peroxide is gradually introduced. During the reaction, which is exothermic intensive cooling is necessary in order to keep the temperature about + 20 °C. Finally, the temperature is reduced to — 2 °C, to enable the major part of the perborate to crystallize. After this operation is finished, the crystals are separated from the mother liquor in a wooden filter press, then washed with water and centrifuged in order to remove the greater part of the moisture, and finally dried in a current of hot air. The mother liquor is returned to the process. The yield of hydrogen peroxide is about 99 per cent and that of borax 97 per cent.

Another way of manufacturing perborate is a process in which sodium peroxide and boric acid are allowed to react with sodium hydrogen carbonate as a neutralizing agent according to the equation:

$$Na_2O_2 + H_3BO_3 + NaHCO_3 + 2\,H_2O = \\ = NaBO_2 \cdot H_2O_2 \cdot 3\,H_2O + Na_2CO_3. \qquad \text{(XXI-3)}$$

The process is carried out in such a way that the boric acid is first dissolved in water, afterwards hydrogen peroxide is introduced to the solution which is intensively cooled to — 2 °C. Finally bicarbonate is added. The crystallized perborate is filtered and dried.

Sodium hydrogen fluoride can be used instead of sodium hydrogen carbonate:

$$Na_2O_2 + H_3BO_3 + NaHF_2 + 2\,H_2O = \\ = NaBO_2 \cdot H_2O_2 \cdot 3\,H_2O + 2\,NaF. \qquad \text{(XXI-4)}$$

*) Milk of silicate is made on the spot by the precipitation of a solution of sodium metasilicate or water glass by sodium or magnesium chloride and by decanting the precipitate.

C. ELECTROCHEMICAL METHOD OF MANUFACTURING SODIUM PERBORATE

1. Theory of electrochemical oxidation

A saturated solution of sodium tetraborate, also containing both carbonate and bicarbonate of sodium, is used as the electrolyte. The presence of excessive solid borax guarantees that the solution is continuously resaturated with this compound during electrolysis. The electrolyte is also saturated with perborate so that this salt, which is formed by anodic oxidation of borax, is separated from the solution immediately after its formation in the form of small crystals.

Carbonate is necessary for electrolysis, as otherwise perborate could not be formed. For this reason its formation is supposed to take place in such a way that sodium percarbonate is first formed at the anode:

$$2\,CO_3^{--} = C_2O_6^{--} + 2e \qquad \text{(XXI-5)}$$

which is hydrolysed with water to give hydrogen peroxide:

$$C_2O_6^{--} + 2\,H_2O = 2\,HCO_3^- + H_2O_2. \qquad \text{(XXI-6)}$$

The hydrogen peroxide then combines with the metaborate ion BO_2^- to form the complex ion:

$$BO_2^- + H_2O_2 = (BO_2 \,.\, H_2O_2)^-. \qquad \text{(XXI-7)}$$

As hydrogen is liberated at the cathode the overall process during electrolysis is expressed by this equation:

$$BO_2^- + 2\,H_2O = (BO_2 \,.\, H_2O_2)^- + H_2. \qquad \text{(XXI-8)}$$

The electrochemical oxidation of sodium tetraborate to perborate is accompanied with a corresponding decrease in alkalinity of the electrolyte i. e. the quantity of carbonate decreases and that of bicarbonate increases during the electrolysis according to the equation:

$$Na_2B_4O_7 \,.\, 10\,H_2O_{(s)} + 2\,Na_2CO_3 + 11\,H_2O = 4\,NaBO_2 \,.\, H_2O_2 \,.\, 3\,H_2O_{(s)} + 2\,NaHCO_3 + 4\,H_2 \qquad \text{(XXI-9)}$$

To maintain alkalinity constant it is necessary to adjust the composition of the electrolyte in regular intervals. This is performed in such a way that a part of the electrolyte is neutralized with sodium hydroxide after the perborate, crystallized from the solution, has been separated on a centrifuge:

$$2\,NaHCO_3 + 2\,NaOH = 2\,Na_2CO_3 + 2\,H_2O \qquad \text{(XXI-10)}$$

This neutralized solution is returned for electrolysis after the content of borax has been supplemented. If the last two equations are added, we obtain the summary equation:

$$Na_2B_4O_7 \,.\, 10\,H_2O_{(s)} + 2\,NaOH + 9\,H_2O = 4\,NaBO_2 \,.\, H_2O_2 \,.\, 3\,H_2O_{(s)} + 4\,H_2, \qquad \text{(XXI-11)}$$

which expresses the total process during the electrochemical manufacture of perborate. Since the mixture of tetraborate and sodium hydroxide in the stoichiometric ratio stated above corresponds to the composition of metaborate, electrolysis can be considered primarily as a process of water decomposition. The oxygen then combines with the metaborate to form perborate, and hydrogen liberated at the cathode escapes into the atmosphere. Of course, this intuitive explanation does not correctly describe the actual process during electrolysis.

Sodium peroxide can also be used to neutralize bicarbonate instead of sodium hydroxide. While this is taking place a certain amount of perborate is simultaneously formed after the necessary quantity of borax has been added. This reaction proceeds according to equation:

$$6\ NaHCO_3 + 4\ Na_2O_2 + Na_2B_4O_7 \cdot 10\ H_2O + 3\ H_2O = \\ = 4\ NaBO_2 \cdot H_2O_2 \cdot 3\ H_2O + 6\ Na_2CO_3 \qquad \text{(XXI-12)}$$

During electrolysis current losses may occur due to secondary processes at the electrodes or to the catalytic decomposition of perborate in solution. In order to reduce undesirable reactions at the anode (e. g. the liberation of oxygen or of carbon dioxide) it is necessary to maintain the carbonate and borax concentration in the solution as high as possible. A still greater influence upon current efficiency has the perborate dissolved in the electrolyte, as with its increasing concentration current efficiency considerably decreases. Although the solubility of perborate in a concentrated solution of normal carbonate and bicarbonate of sodium is comparatively small (about 5 g per litre at 11 °C), actually, perborate can easily form an oversaturated solution containing 7 g per litre which will cause a great decrease in current efficiency.

Current efficiency increases when the temperature of the electrolyte decreases. In spite of this, the electrolyte is not cooled below + 10 °C in practice, because at a lower temperature the conductivity of the electrolyte is reduced and, consequently, the consumption of energy does not diminish but actually increases. At a too low temperature there is also the danger that solid carbonate and bicarbonate will separate from the solution.

Smooth platinum is the only suitable material for anodes as it has a high oxygen overvoltage; for better durability of the anode, pure platinum is not used but an alloy which contains 5 per cent iridium. Current efficiency decreases considerably if there is the slightest trace of any impurity deposited on the platinum such as lead dioxide, manganese dioxide, ferric oxide etc.

In order to limit the reduction of perborate at the cathode alkali metal chromate or bichromate (to achieve a concentration of about 0.3 g. CrO_3 per litre) is added to the electrolyte. Apart from this, a too low current density, below 10 A/sq.dm, should not be used at the cathode.

The stability of the perborate in the electrolyte depends on the presence of catalytically active poisons and on the temperature and concentration of the solution. If the temperature is increased by 10 °C, the rate of decomposition is more

than doubled. As far as the influence of the concentration is concerned it can be stated that the loss caused by catalysis is proportional to the quantity of perborate dissolved in the electrolyte. Ferric oxide is the best known catalyst, which promotes the decomposition of perborate; its influence is evident already in a concentration of 1×10^{-4} per cent. The influence of manganese dioxide is even more harmful as it causes perborate to decompose if present in a concentration of 1×10^{-6} per cent. Other substances which are not so harmful are copper oxide, finely dispersed platinum, cobalt monoxide, etc.

Stabilizers must be used to compensate the influence of the catalyst mentioned, which not only prevent the decomposition of perborate during manufacture but also greatly increase the stability of the final product during storage. The efficiency of these substances is explained by their ability to adsorb colloidally dispersed impurities from the solution, promoting catalytic decomposition of the perborate. Magnesium silicate has proved to be the best stabilizer and it is added to the electrolyte as suspension known as milk of silicate. Its concentration in the electrolyte is kept approximately at a constant level of about 0.5 g. $MgSiO_3$ per litre by continually adding milk of silicate to the electrolyte.

2. The industrial manufacture of perborate

Electrolysis takes place in a concrete or iron tank lined with rubber and equipped with a rubber lined iron stirrer and with aluminium coils through which an aqueous solution of glycerine is circulated, cooled in an ammonia cooling equipment (see Fig. 148). In a cell for a load of 6700 to 7000 A two electrode assemblies are suspended carried by current conductors; these assemblies consist of 21 platinum-irridium gauzes acting as anodes and 22 nickel--plated steel cathodes. The external dimension of one assembly, in which the vertical electrodes are placed 3 mm apart, is 250 × 260 × 260 mm. During electrolysis the liquor enters the bottom part of the assembly and is raised upwards by the liberated gases and leaves the assembly at the top; this circulation of the electrolyte is aided by a stirrer.

The platinum anodes are pressed together in a way similar to the frames of a filter press (see Fig. 148 *c* and *e*), each gauze being separated from the next one by two spacers made of rubber coated zinc, which are placed along the sides of the electrode gauzes (see Fig. 148 b). The whole block of stratched platinum gauzes is bolted between two supporting nickel plated steel frames by nickel bolts. Both terminal zinc spacers are connected to the positive pole of the current source. Between the anodes so arranged nickel plated steel cathodes are inserted alternately (see Fig. 148 f). The cathode plates again are bolted together and fixed to the electrode assembly from which they are insulated. They are provided with lugs and connected to the negative pole of the current source by rubber coated conductors. All parts of the electrode assembly are coated with rubber, except the contact surfaces, and the whole after being assembled together is coated with celulose lacquer in order to protect it against

the corrosive affect of the electrolyte. Current density at the anode is about 40 A/sq. dm., on the cathode 15 to 20 A/sq. dm.

The operation is semi-continuous. During the electrolysis the solution is cooled to about 11 to 12 °C, the solid sodium tetraborate with which the electrolyte is continuously resaturated is maintained in suspension by stirring; the

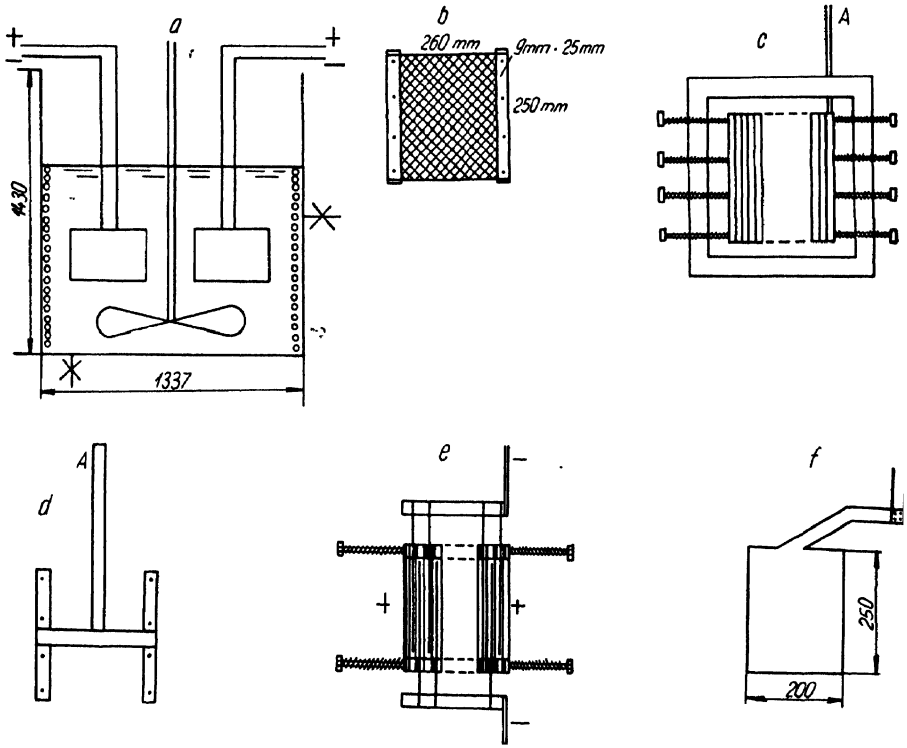


Fig. 148. Electrolyzer for the manufacture of perborate.

a — Electrolytic tank with cooling coil, stirrer and two electrode assemblies. *b* — Platinum-irridium gauze anode with two rubber coated zink spacers. *c* — Assembly of anodes and cathodes bolted together in a frame. *d* — Current conductors to the anodes, *e* — A set of anodes and cathodes which form an electrode assembly, *f* — Nickel plated steel cathode with current conductor.

perborate crystallized from the solution is thus also prevented from settling. At the end of each cycle lasting 12 hours, there is about 270 kg of produced perborate dispersed in 1200 litres of the electrolyte. Then one half of the electrolyte is drained off through a valve which is approximately in the middle of the cell, so that the electrodes in the lower half of the cell remain immersed in the electrolyte and electrolysis continues without interruption. The drained-off electrolyte is replaced by the regenerated make-up solution, in which the

bicarbonate present has been converted to normal sodium carbonate by neutralisation with sodium hydroxide.

The necessary amount of borax, as well as a certain quantity of a suspension of magnesium silicate which acts as stabilizer, are introduced simultaneously. After 6 hours a further charge of borax is added into the cell. After another 6 hours half of the electrolyte is again drained off and the whole operation described above is repeated. The voltage across the bath varies between 5.6 and 6 V and a daily output of 260—270 kg of perborate per cell corresponds approximately to a 57 % current efficiency. The total energy consumption per 100 kg of perborate equals 375 to 390 kw-hr. representing an energy efficiency of about 15 %.

After a 12 hours production cycle the liquor which is drawn off from the cell is centrifuged in an apparatus fitted with nickel screens. The separated mother liquor contains approximately 105 g. Na_2CO_3, 60 g. $NaHCO_3$, 20 to 25 g. $Na_2B_4O_7 \cdot 10\ H_2O$ and 0.5 g. of active oxygen in the form of perborate per litre. A small portion of the mother liquor (5 to 10 per cent) is returned directly to the cell, but the major portion is regenerated and purified. This is done by the addition of a small excess of sodium hydroxide and of a small amount of soda ash to compensate for the loss in carbon dioxide, caused by the decomposition of carbonate at the anode. This operation is carried out in a neutralizer provided with a stirrer and heating coil. After neutralisation has been carried out, the solution is heated to about 70—80 °C and the suspension of magnesium silicate is added to the stirred solution, in order to remove any impurities from the mother liquor. The solution is allowed to settle and the deposit formed is filtered on a filter press. The clear liquor which contains about 165 g/l Na_2CO_3, 6 g/l of free NaOH and 20—25 g/l $Na_2B_4O_7 \cdot 10\ H_2O$ (the perborate was destroyed during the regeneration process) is pumped into a container from which it is charged into the cells. The remaining slurry which contains platinum is collected, dried and shipped to a refinery where the platinum is recovered.

The separated crystalline perborate is dried in a current of air preheated in a heater to 60—70 °C. The Büttner dryer is very suitable for this operation. The dry perborate powder entrained is separated from the air in a cyclone, then homogenized in mixers and finally screened.

As the cooling efficiency of the coil in the cell is reduced with time due to the deposit of salts, it is necessary to discontinue the normal operation of the electrolyzer (at intervals of 3—6 weeks) in order to remove the salt deposit on the cooling coil by dissolving in water.

D. USE OF PERBORATE

Perborate is packed in galvanized steel, or wooden, paper lined drums. The commercial product has 97 to 98% $NaBO_2 \cdot H_2O_2 \cdot 3\ H_2O$, the remainder is sodium tetraborate and carbonate; the content of active oxygen varies between 10.1 and 10.2 per cent.

Whereas by the chemical method it is possible by proper keeping of suitable reaction conditions (low temperature, rapid cooling, intensive mixing during the reaction) to prepare a light product with a bulk density of 0.42—0.55 kg per litre, electrolytic perborate is a heavy product of the bulk density 0.8 to 1.0 kg. per litre. Consumers frequently prefer the lighter grade of perborate because this product when mixed with other powder substances (i. e. with soap powder) will not become segregated from them even after long storage and especially during transport.

Owing to its oxidizing properties perborate is chiefly used for washing and bleaching wool, artificial silk, velvet, plush, felt, horn, bones, oils, fats, waxes etc.

Mixtures with soap powder, soda ash, water-glass or sodium phosphate are also marketed. The advantage of these powders is the lower soap consumption and fabrics washed in them wear longer than when soda ash is used. In medical science perborate is used for oxygen baths and certain antiseptics.

1. Chemical oxidation

Chlorine or permanganate may be used for chemical oxidation. The first method proceeds according to equation:

$$2\,K_4Fe(CN)_6 + Cl_2 = 2\,K_3Fe(CN)_6 + 2\,KCl. \qquad \text{(XXIV-4)}$$

This method has a disadvantage as the product entrains potassium chloride the removal of which constitutes a very difficult and laborious operation.

The second method starts with a poorly soluble calcium-potassium ferrocyanide $CaK_2Fe(CN)_6$ which is oxidized in water suspension at 80 °C by permanganate in the presence of potassium carbonate and with carbon dioxide bubbling through the solution. The reaction proceeds according to equation:

$$3CaK_2Fe(CN)_6 + KMnO_4 + K_2CO_3 + 2CO_2 = 3K_3Fe(CN)_6 + MnO_2 + 2CaCO_3. \qquad \text{(XXIV-5)}$$

The manganese dioxide and calcium carbonate are allowed to settle and are separated by filtration; the solution is then evaporated and the ferricyanide is allowed to crystallize. The process is fairly complicated and production costs are comparatively high.

Electrochemical oxidation

rochemical oxidation is performed in an electrolyzer with a diaphragm. · anode and an iron cathode are used; the catholyte is a 1—5 per cent solution of potassium hydroxide, the anolyte is a concentrated ferrocyanide solution. During electrolysis hydrogen is liberated at the cathode:

$$2H_2O + 2e = 2H_2 + 2OH^- \qquad \text{(XXIV-6)}$$

while at the anode ferrocyanide is oxidized to ferricyanide:

$$2Fe(CN)_6^{----} = 2Fe(CN)_6^{---} + 2e. \qquad \text{(XXIV-7)}$$

The process in the electrolyzer can be summarized by the following equation:

$$2K_4Fe(CN)_6 + 2H_2O = 2K_3Fe(CN)_6 + 2KOH + H_2 \qquad \text{(XXIV-8)}$$

It is clear from this equation that for each mole of ferricyanide formed one mole of potassium hydroxide is also formed whereby the alkalinity of the electrolyte increases during electrolysis. It has been ascertained by experiments that after the finished oxidation, 40 per cent of the total amount of hydroxide formed remain in the cathode compartment while the other 60 per cent are transferred into the anolyte by migration of hydroxyl ions.

The standard equilibrium potential at the anode related to reaction (XXIV-7) is $\pi^\circ = 0.356$ V. As oxygen is evolved owing to overvoltage from neutral solutions as late as the potential is about 1.2 V and from alkaline solution at about 0.8 V, the oxidation of ferrocyanide to ferricyanide can proceed with a 100 per

cent efficiency until the ratio of concentration of ferrocyanide to ferricyanid drops and, consequently, the anode potential increases up to the deposition potential of oxygen. This in turn is lowered during electrolysis due to the increasing concentration of hydroxide. The liberation of oxygen is aided at the same time by concentration polarization which may be suppressed by using a low current density at the anode, stirring the electrolyte and working at a higher temperature. The material for the anode is irrelevant as far as current efficiency is concerned, unless the anode becomes coated by a film of insoluble substances formed by the dissolution of a small amount of anode metal and its precipitation in the alkaline medium in the form of hydroxide. Some metals do not become coated in this way e. g. platinum, gold, nickel and cobalt. Thus at electrodes made of these metals reaction (XXIV-7) proceeds reversibly at a lower current density while at a higher current density only concentration polarization occurs. If, however, iron, lead, silver or zinc are used as anodes they become coated with a poorly soluble layer which causes a considerable rise of potential; this results in the simultaneous liberation of oxygen and a great drop in current efficiency. A potential rise can occur even with a nickel anode, which is commonly used for ferricyanide production if electrolysis proceeds at a temperature above 50 °C. Under these conditions the ferricyanide formed is already decomposed by the hydroxide accumulated in the anolyte, due to the migration of hydroxyl ions toward the anode; the ferric hydroxide formed in this reaction then envelops the anode. On the other hand the temperature used for electrolysis should not be much below 50 °C as at a lower temperature the diffusion of ferrocyanide ions from the bulk of the solution towards the anode is slower and the possibility of a premature liberation of oxygen is greater.

The lower the current density at the anode the greater the portion of ferrocyanide ions oxidized to ferricyanide ions with 100 per cent current officiency. This can be seen from the following table related to electrolysis, which was carried out at 18 °C with a smooth nickel anode and a solution containing 0.5 mole of $K_4Fe(CN)_6 \cdot 3H_2O$ per litre.

Current density A/sq. dm²	2	1,5	1,0	0,5
Amount (in per cent) of $K_4Fe(CN)_6 \cdot 3H_2O$ oxidized with 100 per cent current efficiency	83.7	87.8	92.6	95.6
Total current efficiency at complete oxidation, in per cent	80.6	83.0	90.5	94.5

It will be seen that even the total current efficiency at the complete oxidation of ferrocyanide increases inversely in proportion to the current density.

These current efficiencies are achieved only when a diaphragm is used to

prevent the cathodic reduction of ferricyanide ions to ferrocyanide ions; if no diaphragm is used, current efficiency drops bellow 50 per cent. The voltage across the electrolyzer should not exceed 3.5 V when a diaphragm is used; if it is higher, the diaphragm becomes clogged with impurities contained in the electrolyte (mainly calcium salts) and must be replaced.

It has already been stated that one cause of oxygen evolution is the depletion of ferrocyanide ions in the solution which takes place towards the end of electrolysis. Therefore, when the electrolyte is continually resaturated with ferrocyanide a high current efficiency can be attained during the entire operational period. In this way the solution may be enriched with ferricyanide, which is more soluble than ferrocyanide, to such an extent that it begins to crystallize in the anode compartment. This is, however, not carried out in practice as it leads to the deposition of crystals on the anode surface, whereby, the voltage is considerably increased.

The anolyte, in which the content of potassium hydroxide increases, must be periodically withdrawn and chemically regenerated. This is best achieved by using the following reaction:

$$CaK_2Fe(CN)_6 + 2KOH + CO_2 = K_4Fe(CN)_6 + CaCO_3 + H_2O, \quad \text{(XXIV-9)}$$

the alkalinity of the anolyte being neutralized by carbon dioxide in the presence of calcium-potassium ferrocyanide. After filtering off the calcium carbonate the clear solution is returned to the process.

According to an older method developed by the firm of *Siemens & Halske* a solution containing 280 g of $K_3Fe(CN)_6$ and 90 g of $K_4Fe(CN)_6$ per litre is electrolyzed at 40—50 °C. The electrolysis is allowed to proceed until the ferricyanide content has risen to 320 grams per litre while the ferrocyanide content has diminished to 50 grams per litre. The electrolyte is then led into a crystallizer where it is stirred and cooled to 18 °C which causes 40 grams of ferricyanide to crystallize from each litre of the liquor. The precipitated crystals of potassium ferricyanide are then separated from the mother liquor, dried and packed. The mother liquor containing 280 g of $K_3Fe(CN)_6$ and 50 g $K_4Fe(CN)_6$ per litre is heated to 40—50 °C, resaturated with potassium ferrocyanide and returned to the process.

The electrolytic vessel is made of stoneware while the diaphragms are made of porcelain. During the operation the electrolyte is stirred to suppress the concentration polarization. Nickel is the best anode material; iron is less suitable as it becomes coated with a non-conducting layer of hydroxide and requires cleaning in order to prevent any rise in the cell voltage. The hydroxide concentration in the anolyte is maitained at about 10 grams of KOH per litre. A 1 to 5 per cent solution of potassium hydroxide is used as the catholyte and the cathodes are made of iron.

The anodic current density is about 1 A/sq. dm. while the cathodic current density may attain four times this value. The voltage varies between 2.5 and 3 V. With a normal ferrocyanide concentration the current efficiency is about

70 per cent which means that 1000 A-hr. are required to produce 8.6 kg of $K_3Fe(CN)_6$ or the production of 1 kg of potassium ferricyanide necessitates 0.35 kw-hr. (using a voltage of 3 V across the cell).

Potassium ferricyanide is used for dyeing and printing of cotton, staining wood yellow, in photography (for copying drawings), for developing blueprints and brownprints and in chemical laboratories.

XXV. REGENERATION OF CHROMIC ACID

To oxidize some organic compounds, e. g. anthracene to anthraquinone, chromic acid or a solution of sodium bichromate in diluted sulphuric acid are used. During the process the chromic acid is reduced according to equation:

$$2H_2CrO_4 + 3H_2SO_4 + X = Cr_2(SO_4)_3 + 5H_2O + (X + 3O); \qquad (XXV\text{-}1)$$

here X stands for the organic compound to be oxidized.

Waste chromium lyes containing chromic sulphate dissolved in sulphuric acid were formerly regenerated by the addition of lime in excess to neutralize the sulphuric acid and precipitate the chromium hydroxide. The precipitate of chromium hydroxide obtained was subject to oxidizing calcination in a rotary furnace and converted to calcium chromate which in turn was converted to sodium bichromate as follows:

$$2CaCrO_4 + Na_2SO_4 + H_2SO_4 = Na_2Cr_2O_7 + 2CaSO_4 + H_2O \qquad (XXV\text{-}2)$$

This process was of course uneconomical because it involved high production costs and high consumption of sulphuric acid. The lye, however, may be electrochemically regenerated in a more simple way by allowing the Cr^{+++} ions to be anodically oxidized according to equation:

$$2Cr^{+++} + 8H_2O = 2CrO_4^{--} + 16H^+ + 6e. \qquad (XXV\text{-}3)$$

At the cathode the hydrogen ions are reduced:

$$6H^+ + 6e = 3H_2. \qquad (XXV\text{-}4)$$

The total process which occurs during the regeneration of chromate lyes can be summarized as follows:

$$2Cr^{+++} + 8H_2O = 2CrO_4^{--} + 10H^+ + 3H_2. \qquad (XXV\text{-}5)$$

From this equation it can be seen that during the regeneration of chromium lyes sulphuric acid, which has been fixed in the form of chromium sulphate during the oxidation of organic compounds, is freed again.

The high value of the potential $\pi^\circ = 1.8$ V related to reaction (XXV-3) justifies in advance the assumption that the oxidation of trivalent chromium ions will be accompanied with an evolution of oxygen chiefly during the final stage of electrolysis, when the majority of Cr^{+++} ions has been oxidized to CrO_4^{--} ions. The material used for the anodes has a great influence upon the oxidation efficiency attained. It has been proved by experiments that oxidation will not occur on smooth platinum anodes at all. On platinum anodes coated with platinum black current efficiency is rather low, while with lead anodes which become coated with lead dioxide during electrolysis it is possible to reach

comparatively the highest efficiency. As there is no substantial difference between the corresponding potentials at platinum and at lead anodes the specific effect of a lead anode is attributed to the lead dioxide formed on the surface of the electrode which mediates the transfer of oxygen:

$$3PbO_2 + 2Cr^{+++} + 2H_2O = 2CrO_4^{--} + 3Pb^{++} + 4H^+. \qquad \text{(XXV-6)}$$

Analogously chromium salt may be oxidized on platinum anodes coated with platinum black by the peroxides of this metal formed during electrolysis.

Large-scale regeneration is carried out in an electrolyzer with lead electrodes while the anolyte is separated from the catholyte by a diaphragm which prevents a cathodic reduction of the chromate ions formed. If a lower current efficiency is acceptable the reduction can be partially suppressed without using a diaphragm by merely using a high current density at the cathode (exceeding 20 A/sq. dm.) and a suitably low concentration of chromic acid (max. 100 g of CrO_3 per litre).

During electrolysis performed with the use of a diaphragm the migration of ions is manifested by a rise of the sulphuric acid content in the anolyte with a simultaneous reducing of its content in the catholyte. Therefore, if diluted sulphuric acid would be always directly introduced into the cathode compartment and spent chromium lye into the anode compartment, the acidity in the regenerated solution would rise not only due to the effect of reaction (XXV-3) but also to migration. Enriching of the anolyte by sulphate ions is analogous to the process encountered in the production of persulphuric acid and persulphates so it can be counteracted by the same methods. The spent chromium lye which has been used for the oxidation of an organic substance is first passed through the cathode compartments of the electrolyzer. After staying a certain time in these compartments the electrolyte loses part of its sulphuric acid which has passed into the anolyte. The solution is then pumped into the anode compartments where oxidation of the trivalent chromium occurs and the amount of sulphuric acid lost in the previous stage by migration from the cathode compartments is restored. The electrochemically regenerated solution in this way maintains its constant composition and is then used for oxidation and the cycle is repeated.

The regeneration is carried out most advantageously in a system of stoneware tubs arranged in a cascade. The tubs are divided by diaphragms into anode and cathode compartments. Lead electrodes are used in both anolyte and catholyte. Each tub is covered by glass and provided with an opening for exhausting the gases and vapours by a fan. The electrolyte first flows through the cathode compartments, then it is collected in a receiver and pumped into the anode compartments for oxidation.

In the older type installations regeneration was performed by a stationary method. Several (e. g. 12) pairs of lead electrodes were suspended in a large tub. Electrodes were cylindrical in shape and provided with holes to facilitate the circulation of the electrolyte. The opposite electrodes were separated by cylin-

drical diaphragms. In this arrangement chromium lyes was first introduced into the cathode compartments (inside the diaphragms) and then pumped into the outer anode compartment.

Before regeneration the electrolyte contains chromic sulphate equivalent to about 100 to 110 grams of CrO_3 and 250 grams of H_2SO_4 per litre. After oxidation, the content of sulphuric acid is raised to some 450 grams per litre. Current density at the anode equals 1 to 3 A/sq. dm; the current efficiency of the process amounts to 70—75 per cent while the degree of oxidation attained is about 85 per cent (the degree of oxidation means the amount — in per cent — of trivalent chromium oxidized to hexavalent). The use of a higher current density at the anode is not recommended because the amount of liberated oxygen will increase while the current efficiency will decrease; apart from this, the temperature of the cell could not be maintained within a desirable range by dissipation of the heat by natural convection and radiation only. The voltage across the cell related to the above-mentioned current density is between 3.2 to 3.6 V, provided a suitable diaphragm is used. The energy consumption under normal operating conditions will be about 3.5 to 4.2 kw-hr. The operating temperature during electrolysis is between 30 and 50 °C.

XXVI. WHITE LEAD

White lead 2 $PbCO_3$. $Pb(OH)_2$, also known as Prussian-, Krems-, Pearl-, Genoan-, Silver-, Snow white etc. is one of the most important white pigments. It forms fine hexagonal crystals, insoluble in water. It is sold in the form of powder, paste or cubes. The colour is bluish-milky white, a shade for which it is especially valued. Its covering power is higher the more its composition approaches that of basic carbonate; normal lead carbonate, on the other hand, is completely unsuitable as pigment.

The normal method of preparation is a chemical one: water vapour and flue gases are allowed to react with lead in the presence of acetic acid or lead acetate. A part of the world production of white lead is produced electrochemically.

In this process basic lead carbonate is formed on dissolving anodically a lead electrode in a solution of sodium carbonate. To prevent this insoluble compound from being deposited at the anode surface, whereby the further dissolution of the lead would be hindered, sodium acetate or chlorate (the dissolving salt) is added to the electrolyte apart from sodium carbonate (the precipitating salt); this has been already mentioned in the theoretical section. Under these conditions soluble lead acetate or chlorate will be primarily formed at the anode, which after diffusing into the bulk of the electrolyte is precipitated by sodium carbonate and hydroxide according to equation:

$$3Pb(C_2H_3O_2)_2 + 2Na_2CO_3 + 2NaOH = 2PbCO_3 . Pb(OH)_2 + 6NaC_2H_3O_2 \qquad \text{(XXVI-1)}$$

It will be seen from this equation that the dissolving component of the electrolyte, i. e. sodium acetate or chlorate, is continually regenerated in the course of the process. The sodium carbonate and hydroxide consumed in the reaction are supplemented by the migration of CO_3^{--} and OH^- ions from the catholyte. At the cathode made of lead or of iron hydrogen is liberated whereby the concentration of hydroxyl ions in the catholyte increases. In order to maintain their concentration within suitable limits and to replace the carbonate ions consumed in the production of white lead the electrolyte is continuously saturated by carbon dioxide thus converting the hydroxide to carbonate.

The oldest electrochemical method is the *Luckow process* using as electrolyte a mixture of 80 parts sodium chlorate and 20 parts sodium carbonate in a 1.5 per cent solution.

The cathode at which the hydrogen is liberated is made of antimonial lead. The electrolyte is maintained slightly alkaline; as during the process a part of it is continually withdrawn, the suspension of the white lead removed by filtration and the filtrate after saturation with carbon dioxide returned to the process.

Electrolysis is performed at a room temperature at a current density of about 0.5 A/sq. dm. and a voltage across the electrolyzer of 2 V. If the amount

of the dissolving salt is decreased or the current density increased above 0.5 A/sq. dm. the lead is rendered passive and liberation of oxygen will occur instead of the anodic dissolution of lead.

A more modern method was developed recently by *Sperry*. Here sodium acetate is used as the dissolving component of the electrolyte instead of sodium

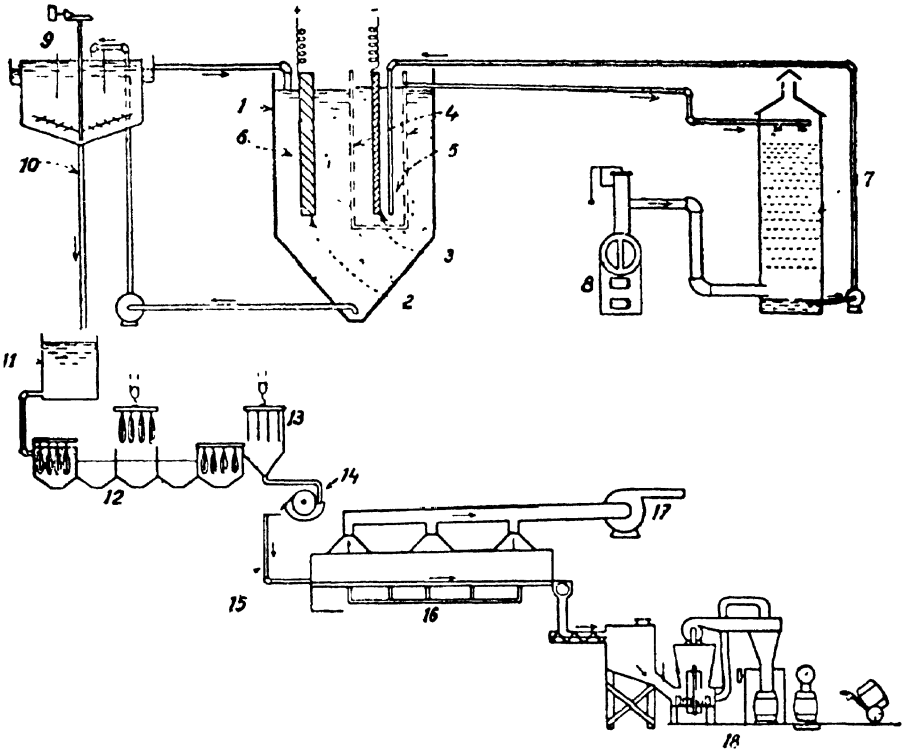


Fig. 149. Schematic representation of Sperry's process for white lead production. *1* — Electrolyzer, *2* — Lead anode, *3* — Iron cathode, *4* — Diaphragm enveloping the cathode, *5* — Catholyte containing OH^- and CO_3^{--} ions, *6* — Anolyte with dispersed white lead, *7* — Tower packed with Raschig rings for resaturation of catholyte with carbon dioxide, *8* — CO_2-generator, *9* — Dorr's thickener, *10* — Drain for thickened pulp from Dorr's thickener, *11* — Pulp storage tank, *12* — Filtering station, *13* — Washing of filter cakes with hot water, *14* — Rotary vacuum filter, *15* — Washed filter cakes to dryer, *16* — Aluminium dryer, heated by steam, *17* — Ventilator for exhausting water vapour, *18* — Installation for grinding, screening and packing of white lead.

chlorate. The flow-sheet of an installation operating according to this method is shown in Fig. 149.

The electrolyzer is a rectangular tank made of concrete (1400×650×850 mm) and coated with asphalt, with an inverted pyramide-shaped bottom. There are 18 lead anodes (780×530×25 mm) and 19 steel plates cathodes (780×

$\times 550 \times 3$ mm) suspended into the electrolyzer. Each cathode is fixed in a frame which is enveloped by a thick linen cloth which acts as a diaphragm. The catholyte is a solution of 4 per cent sodium acetate and 3—5 per cent sodium carbonate with a small content of sodium hydroxide. The anolyte contains 4 per cent sodium acetate, 0,06-0.2 per cent sodium carbonate and some 0.05 per cent sodium hydrogen carbonate. It will be seen that the anolyte contains only a very small amount of sodium carbonate; the concentration of the latter is maintained constant during electrolysis by the migration of CO_3^{--} ions from the catholyte.

In order to keep the concentration of the catholyte at a constant level it is circulated and adjusted as follows: the regenerated catholyte is led to each cathode frame by means of a distributing pipe at a rate of 13 litres per minute; it flows upward around the cathode and leaves at the bottom of the frame, depleted of CO_3^{--} ions and enriched in OH^- ions; from there it is pumped to the top of the carbonating tower (see Fig. 149). There it flows down countercurrently to a stream of carbon dioxide which is introduced at the bottom of the tower; the hydroxide is converted to carbonate and the composition of the initial electrolyte thus restored. For saturation, a mixture of carbon dioxide with air is used which contains some 12 per cent CO_2. This mixture is prepared by burning coke and removing the dust and sulphur dioxide from the flue gas. The regenerated solution is recycled to the cathode compartments. The anolyte is circulated in a similar way. It flows at a rate of some 65 litres per minute into the anode compartment, passes along the anodes and is drawn off at the bottom of the electrolyzer tank. The electrolyte leaving contains about 0.5 per cent white lead which remains in suspension at this rate of flow. Later the anolyte passes through a Dorr thickener where the white lead is separated and the clear anolyte recycled to the electrolysis. The thickened pulp from the Dorr apparatus which contains about 25 per cent white lead is filtered and washed countercurrently with water to remove the remaining anolyte, which is then recycled. The filter cakes are washed once again by suspending them in hot water, the white lead is filtered off and dried in an aluminium dryer, heated by steam to 120 °C, ground and finally packed. The product contains about 80 per cent lead and 11 per cent of carbon dioxide.

This method has a great advantage as lead of any grade may be used; the impurities which are more noble than the lead itself, and for this reason cannot be anodically dissolved form a porous metallic slime on the surface of the anode which will be removed at regular intervals. For this reason electrolytically manufactured white lead has a higher degree of purity than that prepared by any chemical method.

Electrolysis is carried out at 40 °C, the current density at the anode being some 3 A per sq. dm and the voltage across the cell 3.5 V. Current efficiency is about 97 per cent and energy consumption amounts to 45 to 50 kw-hr. per 100 kg of white lead produced.

By adjusting the ratio of concentrations of the acetate to the soda as well

as by choosing suitable operating conditions for electrolysis the chemical composition of the product and its physical properties (shape and size of particles) may be varied. White lead pigment produced electrochemically is characterized by a great covering power, an extraordinary degree of purity, homogenity, fineness of grain and whiteness. The size of the grain ranges between 0.95 and 1.84 microns, the density of the product equals 6.81; the consumption of oil is 8.35 to 14.00 millilitres per 100 grams of white lead. The product usually contains no acetic acid, no metals (except lead) and has a maximum of 0.02 per cent soluble constituents.

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